

Strukturaufklärung in der molekularen anorganischen Chemie

9. Gasphasen-Elektronenbeugung

Gasphasen-Elektronenbeugung

| | Hard X-ray | Soft X-ray | Vacuum UV | Near UV | Visible blue red | Near IR | Mid IR | Far IR | Sub-mmwave | mm-wave | Micro-wave | Radio-wave | |
|--------------|---------------------|--------------------|--------------------|----------------------|----------------------|--------------------|----------------------|----------------------|------------|--------------------|------------|----------------------|--------------------------------|
| \leftarrow | $< 0.1 \text{ \AA}$ | 5 \AA | 100 \AA | 2000 \AA | | 0.7 μm | 2.5 μm | 25 μm | | 1 mm | | 10 cm | \rightarrow |
| | | | 10 nm | 200 nm | 400 nm | 700 nm | 2500 nm | | | | | | |
| | $> 10^9$ | 2×10^7 | 10^6 | 5×10^4 | 2.5×10^4 | 1.4×10^4 | 4000 | 400 | | 10 | | 0.1 | $\tilde{\nu} / \text{cm}^{-1}$ |
| | 1.2×10^7 | 2.4×10^5 | 1200 | 600 | 300 | 170 | 48 | 4.8 | | 0.12 | | 1.2×10^{-3} | $E / \text{kJ mol}^{-1}$ |
| | 120 000 | 2400 | 120 | 6 | 3 | 1.7 | 0.5 | 0.05 | | 0.001 | | 0.00001 | E / eV |
| | 3×10^{19} | 6×10^{17} | 3×10^{16} | 1.5×10^{15} | 7.5×10^{14} | 4×10^{14} | 1.2×10^{14} | 1.2×10^{13} | | 3×10^{11} | | 3×10^9 | ν / Hz |

Gasphasen-Elektronenbeugung \equiv Gasphasen-Elektronendiffraktion (GED)

Ultrafast Gasphasen-Elektronendiffraktion (UED)

λ : $\sim 0.05 \text{ \AA}$ (GED); $\sim 0.003 \text{ \AA}$ (UED)

Charakteristische Zeit: $\sim 10^{-18}$ Sek.

GED

Wechselwirkung mit Strahlung:

- (Optische/Radio) Spektroskopie
- Streuung/Diffraktion
- Resonanzmethode
- Elektrische Methode
- Ionisation

Probe Beeinflussung:

- Destruktiv
- Nicht destruktiv

Anwendung:

- Identifizierung/Sauberkeit
- Elementaranalyse
- Chemische Gruppen
- Chemische Konnektivität
- Konformations-Eigenschaften
- Symmetrie
- Geometrie (Längen, Winkel)
- Schwingungen
- Elektronische Struktur (/Dichte)
- (Elektrische) Dipolmomente

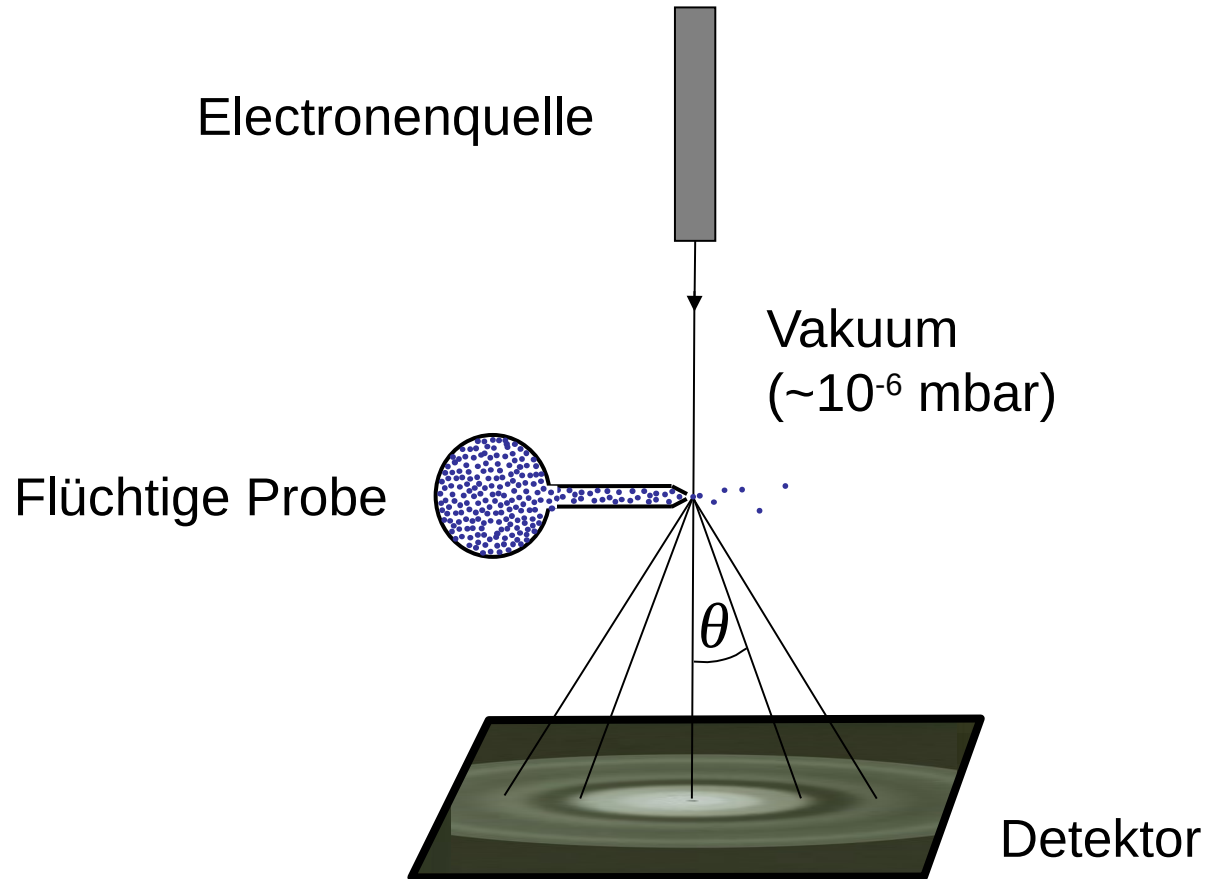
Charakteristische Zeit:

- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

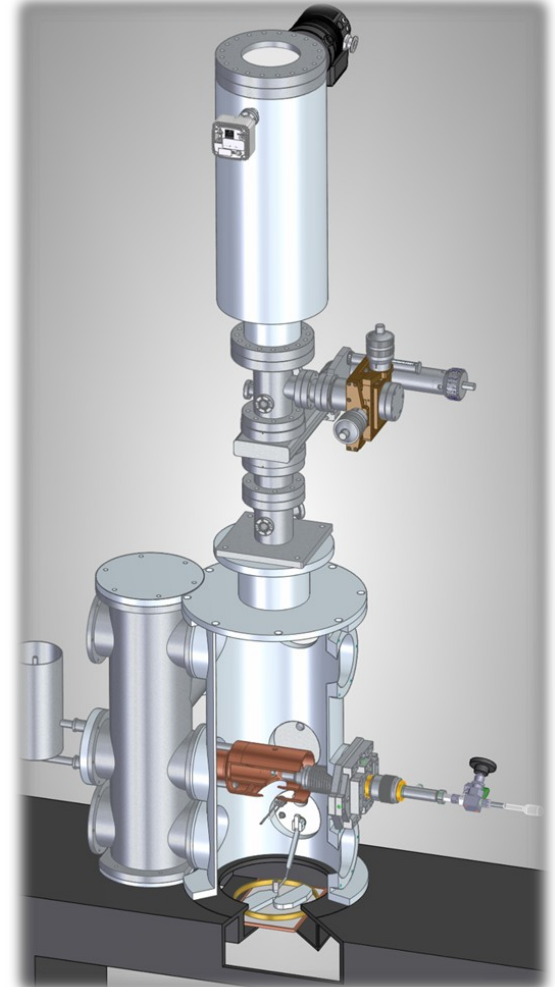
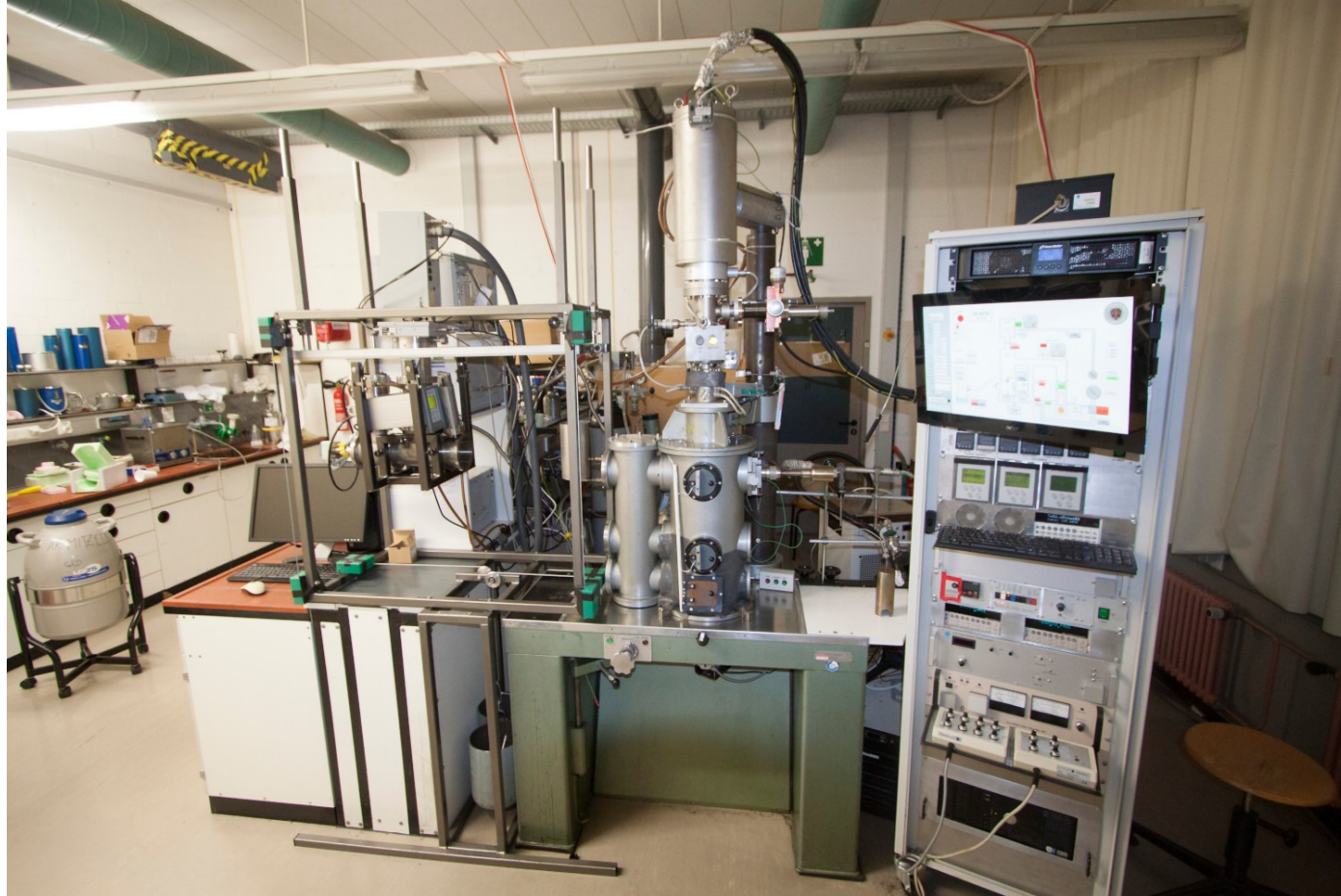
Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

GED: prinzipielles Schema

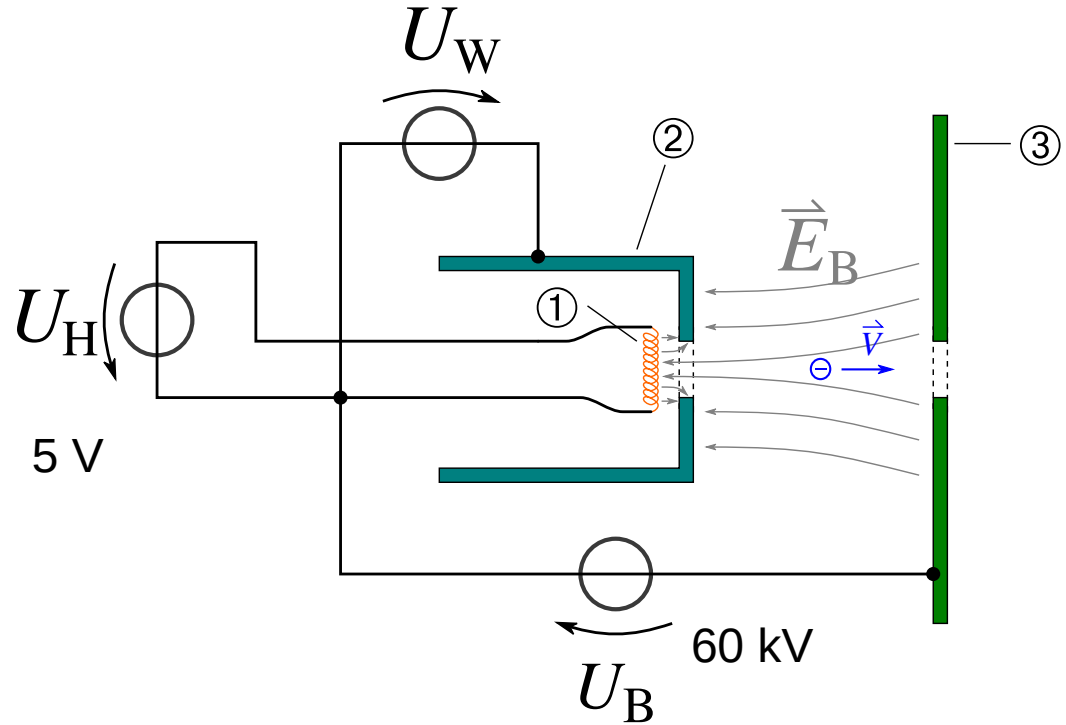
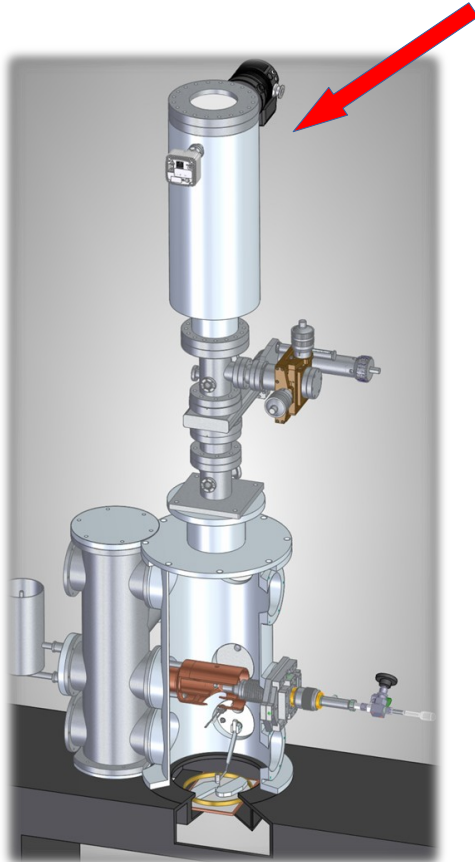


GED in Bielefeld



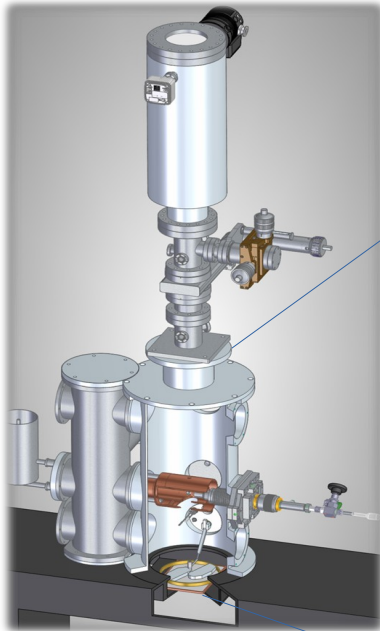
Y. V. Vishnevskiy et al., *Rev. Sci. Instrum.* 2020, 91, 073103.

Elektronenquelle

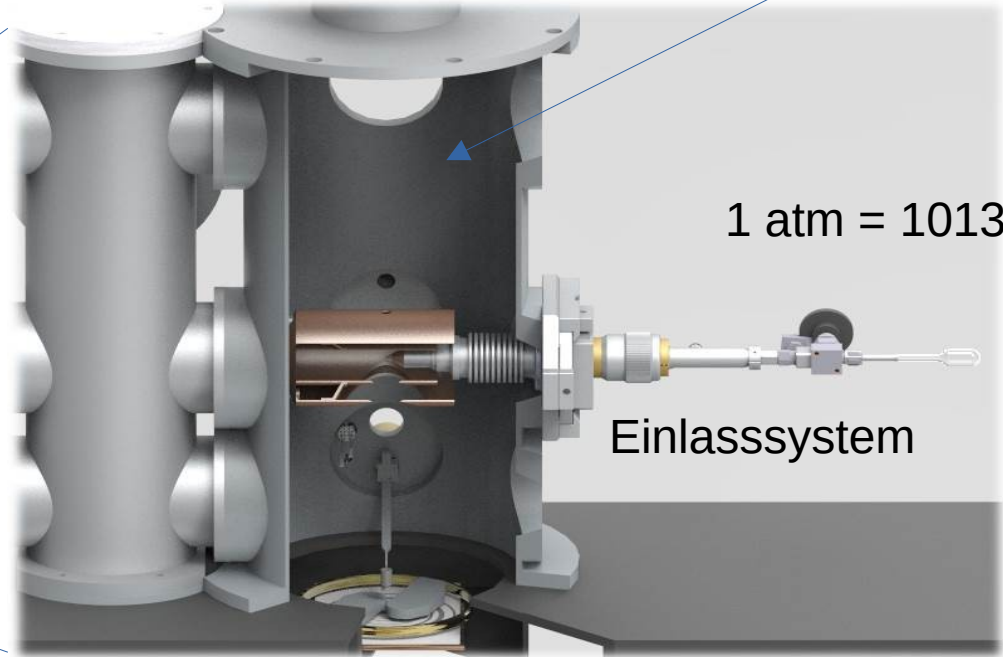


- ① Glühkathode
- ② Wehneltzylinder
- ③ Anodenblende

Diffraktionskammer

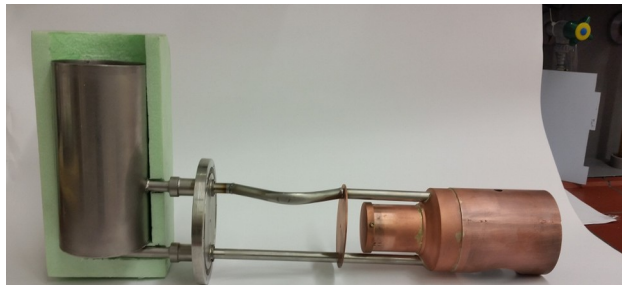


Hochvakuum 10^{-7} mbar



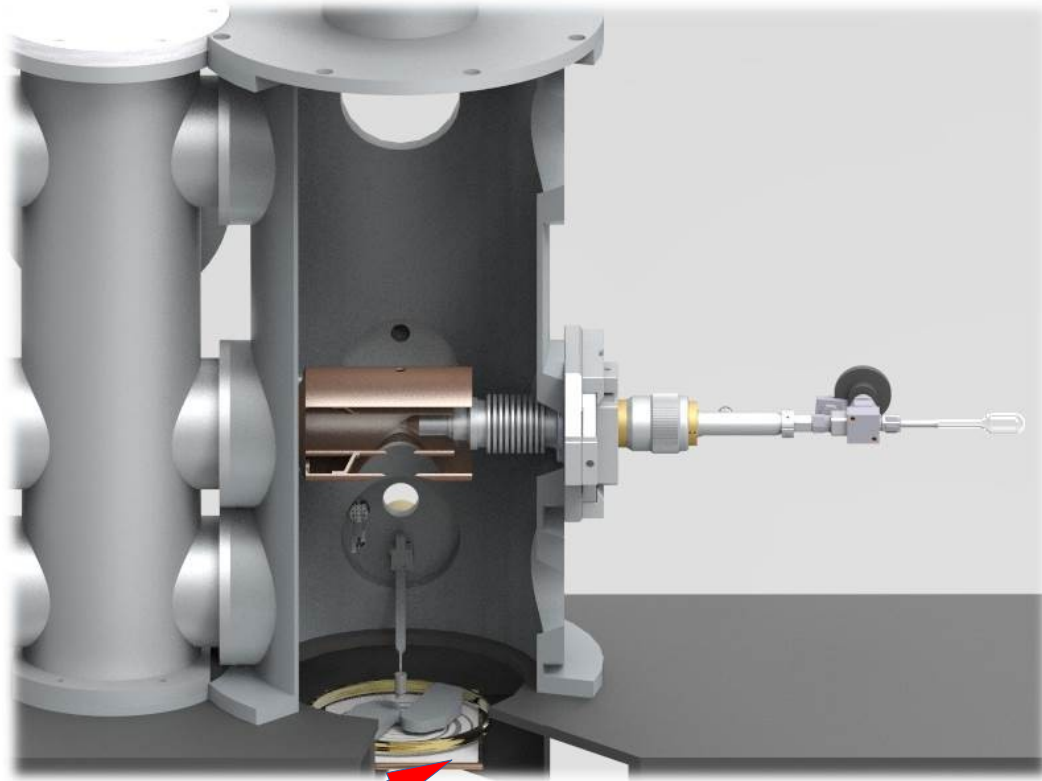
1 atm = 1013.25 mbar

Einlasssystem



Kühlfalle für flüssigen N_2 (77.355 K = -195.795 °C)

Detektorsystem



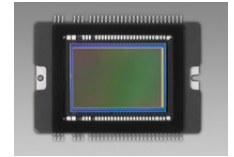
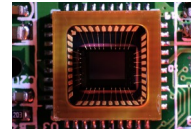
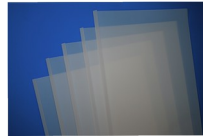
Detektor

Detektorsystem

CCD – Charge-coupled device

IP – Imaging plate

CMOS – Complementary metal-oxide-semiconductor



| | Photo | CCD | IP | CMOS |
|------------------|-------|-----|-----|------|
| Auflösung | + | +/- | +/- | - |
| Dynamic range | -- | +/- | + | ++ |
| Empfindlichkeit | +/- | + | + | ++ |
| Größe | ++ | -- | + | + |
| Ablesung | -- | + | +/- | + |
| Wiederverwendung | -- | ++ | + | ++ |
| Preis | ++ | +/- | +/- | -- |

Imaging Plate Detektor

Imaging plates: Flexible Polyester-Basis überzogen mit hochdisperssem Bariumfluorohalogenid dotiert mit Eu^{2+} [$\text{BaF}(\text{Br},\text{I}):\text{Eu}^{2+}$]

Die Elektronenenergie wird in Form von „trapped electrons“ als angeregte 'F-Zentren' und Eu^{2+} -Ionen-Löchern gespeichert.

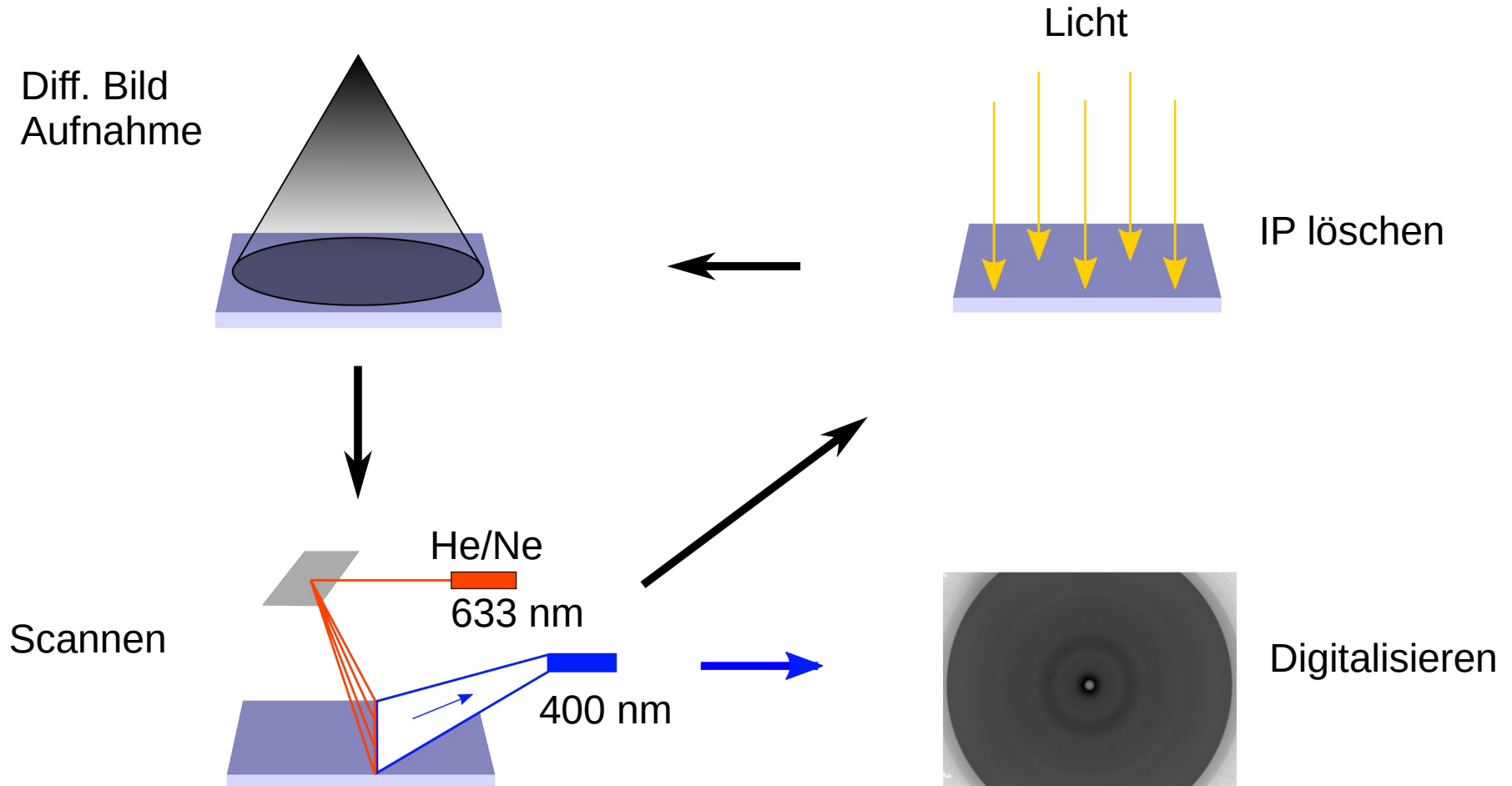
F-Zentren: Absorption ~ 600 nm

Scannen: (He-Ne-Laser 633 nm)
„trapped electrons“ werden freigesetzt und vereinigen sich mit den Eu^{2+} -Löchern.

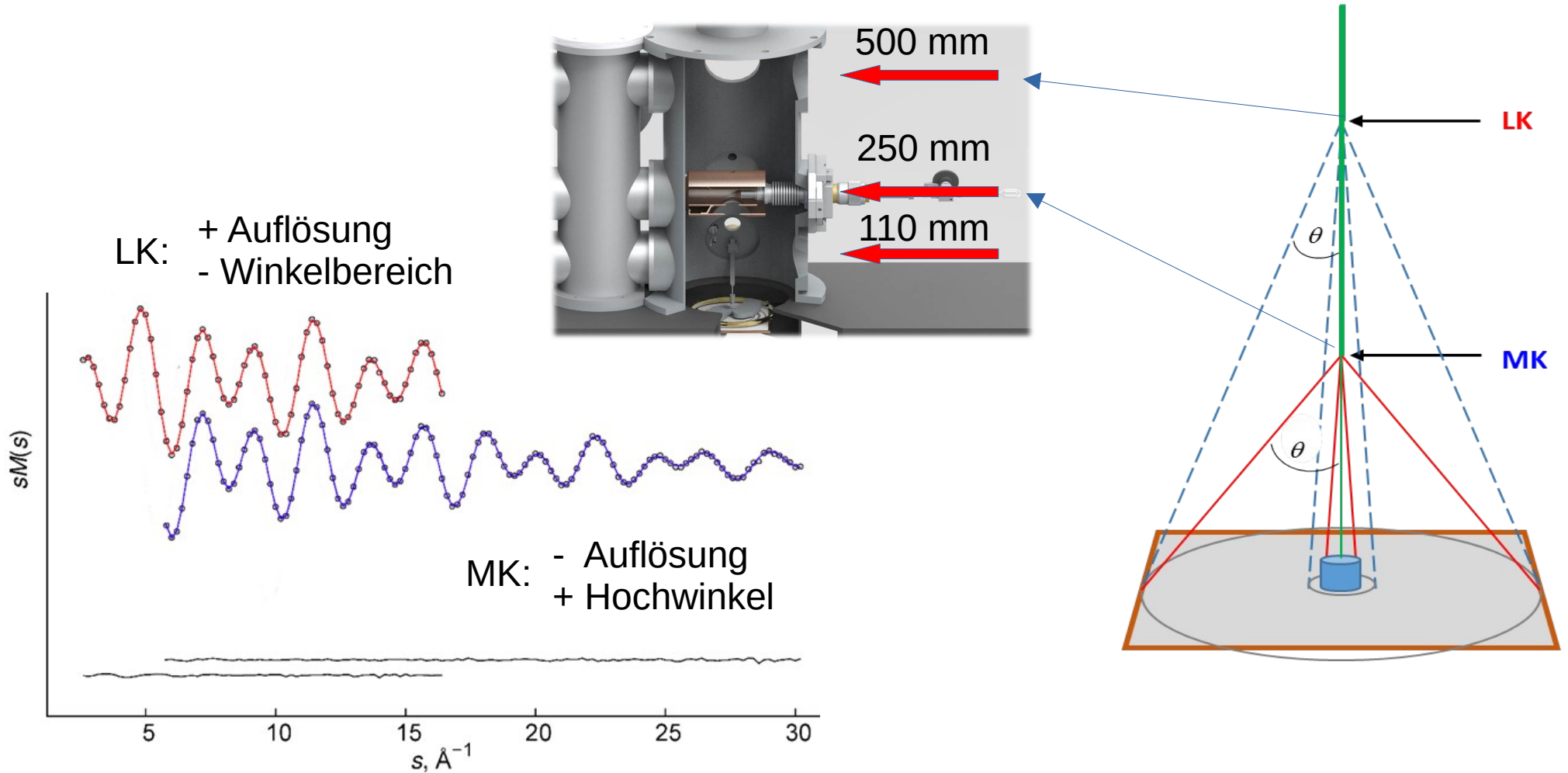
Photonen von ~ 400 nm werden emittiert, d. h. photo-stimulierte Lumineszenz.



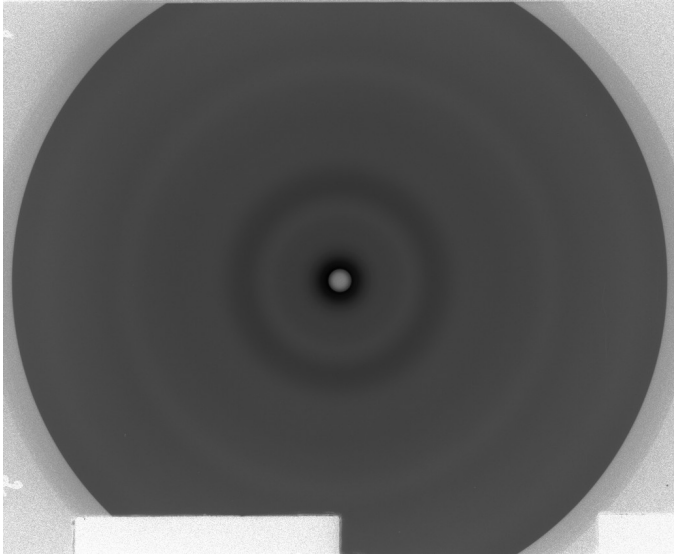
Messungen auf IPs



Kameraabstände

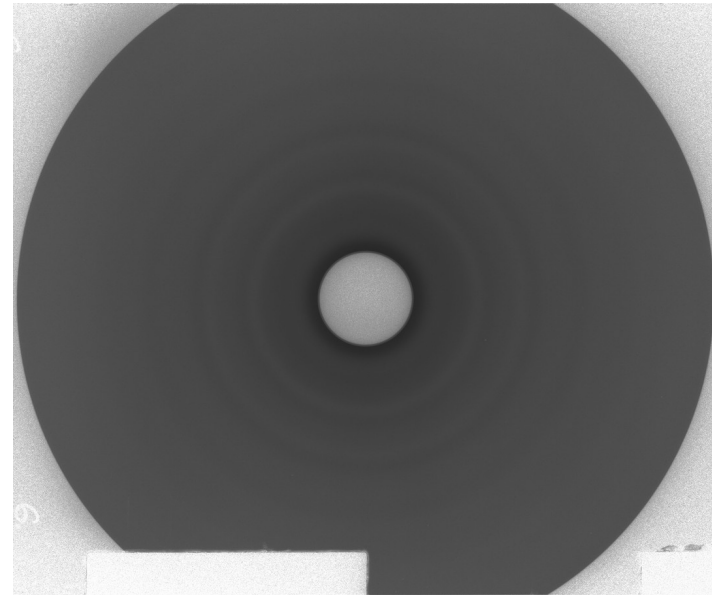


Beugungsmuster: C₆H₆



LK ($L = 500$ mm)

MK ($L = 250$ mm)



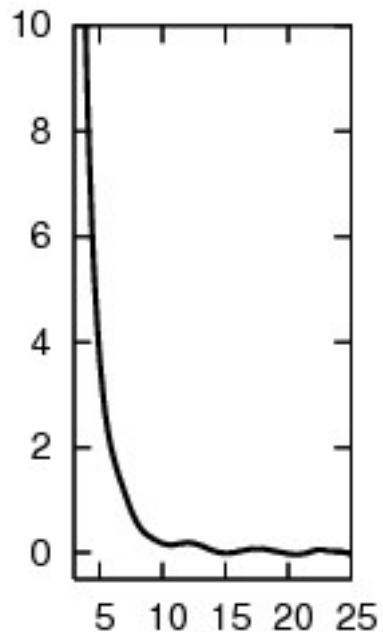
Vom Beugungsbild zu I_m

$$I = I_a + I_m + I_{\text{background}}$$

atomarer Beitrag
molekularer Beitrag



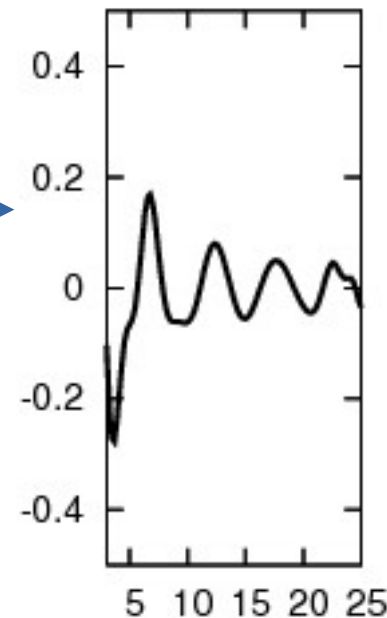
Daten-
reduktion
 $\theta \leftrightarrow s$



Gesamte Intensität

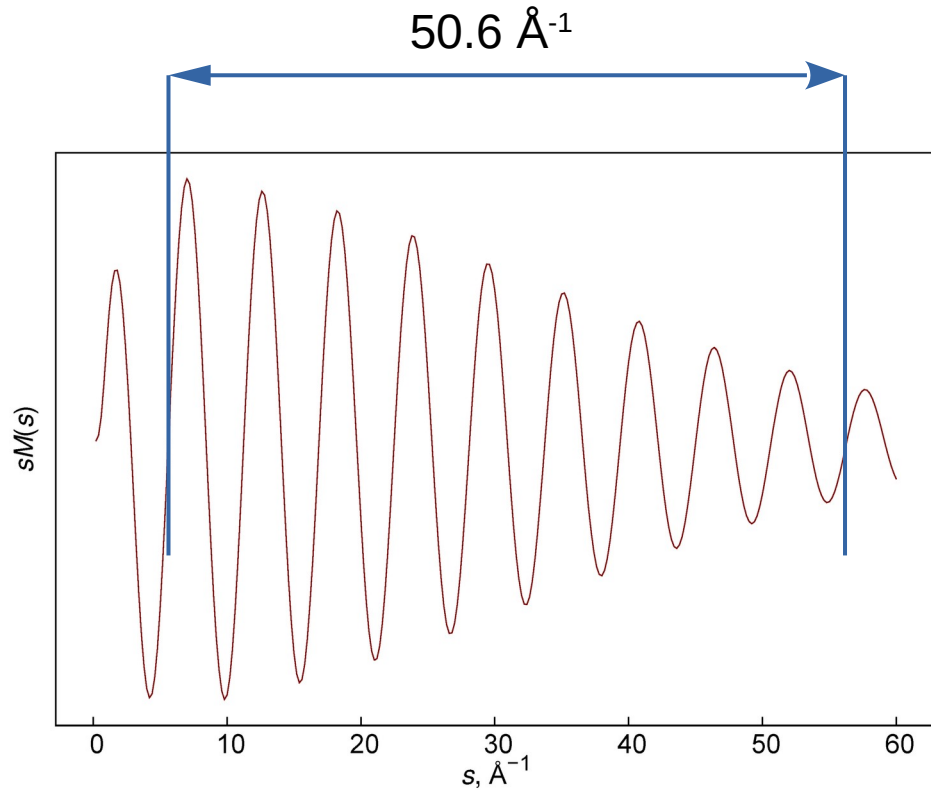
$-I_a, -I_b$

$$sM(s) = \sum_{i>j} g_{ij} e^{-\frac{l_{ij}^2 s^2}{2}} \frac{\sin(sr_{ij})}{sr_{ij}}$$



Molekular-Intensität

Ein Abstand: N₂



$$sM(s) = g_{NN} e^{\frac{-l^2 s^2}{2}} \frac{\sin(sr)}{sr}$$

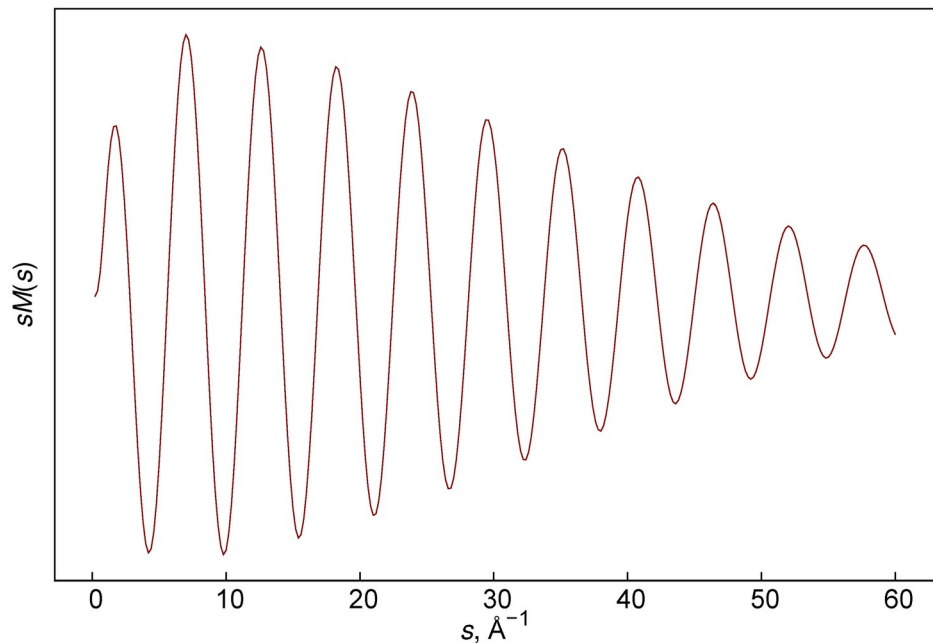
Eine Periode = $50.6/9 = 5.62 \text{ \AA}^{-1}$
Frequenz = $2\pi/5.62 = 1.12 \text{ \AA}$

$$r(\text{N-N}) = 1.12 \text{ \AA}$$

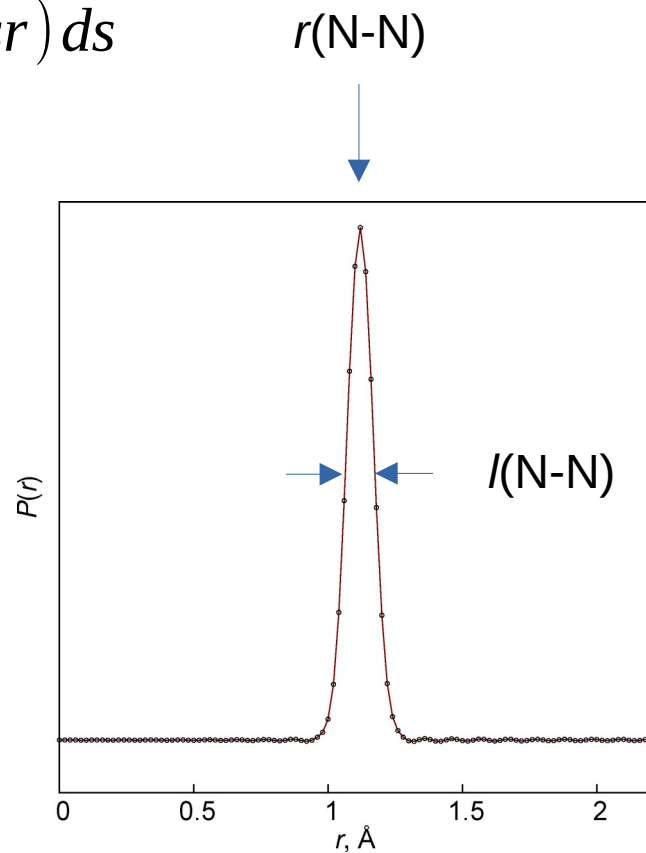
Fourier-Transformation: RDF

$$sM(s) = g_{\text{NN}} e^{-\left(\frac{l^2 s^2}{2}\right)} \frac{\sin(sr)}{sr}$$

$$P(r) = \int_0^{\infty} sM(s) \sin(sr) ds$$

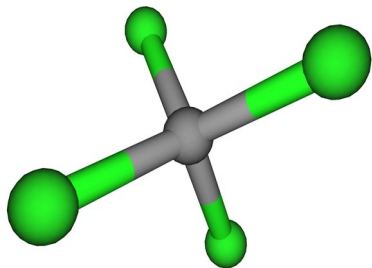


sin-FT 



Radial distribution function (RDF)

Zwei unterschiedliche Abstände: CCl₄

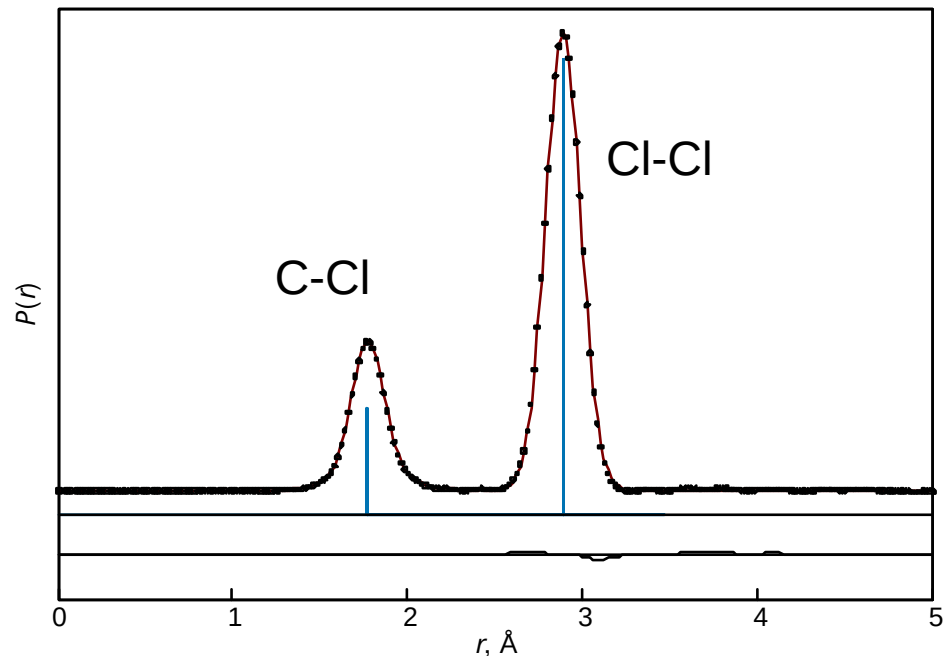
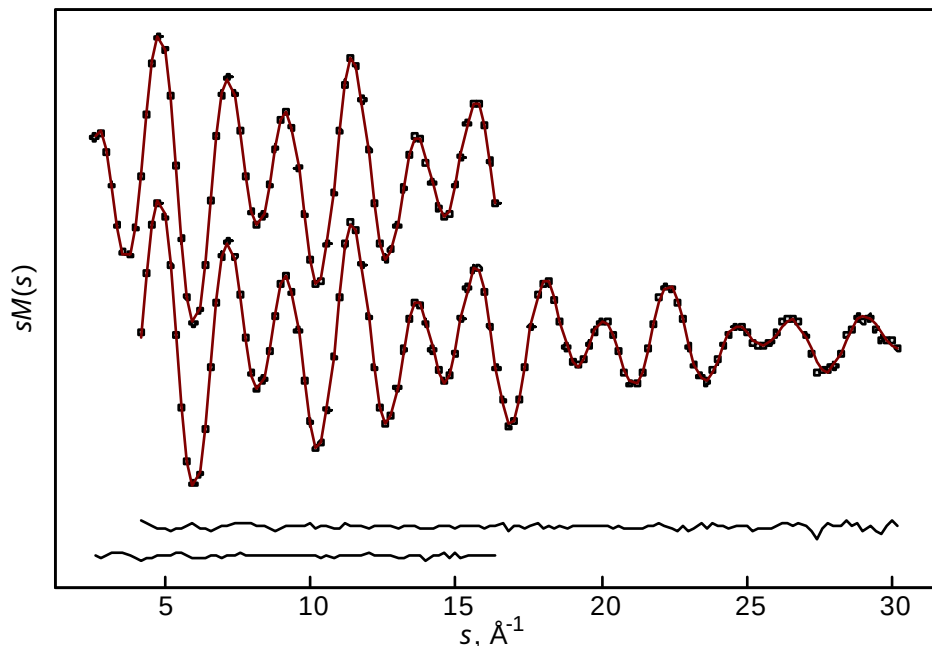


$$r(\text{C}-\text{Cl}) = 1.7663(3) \text{ \AA}$$

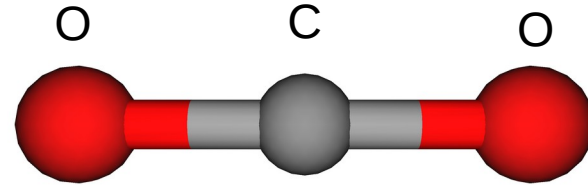
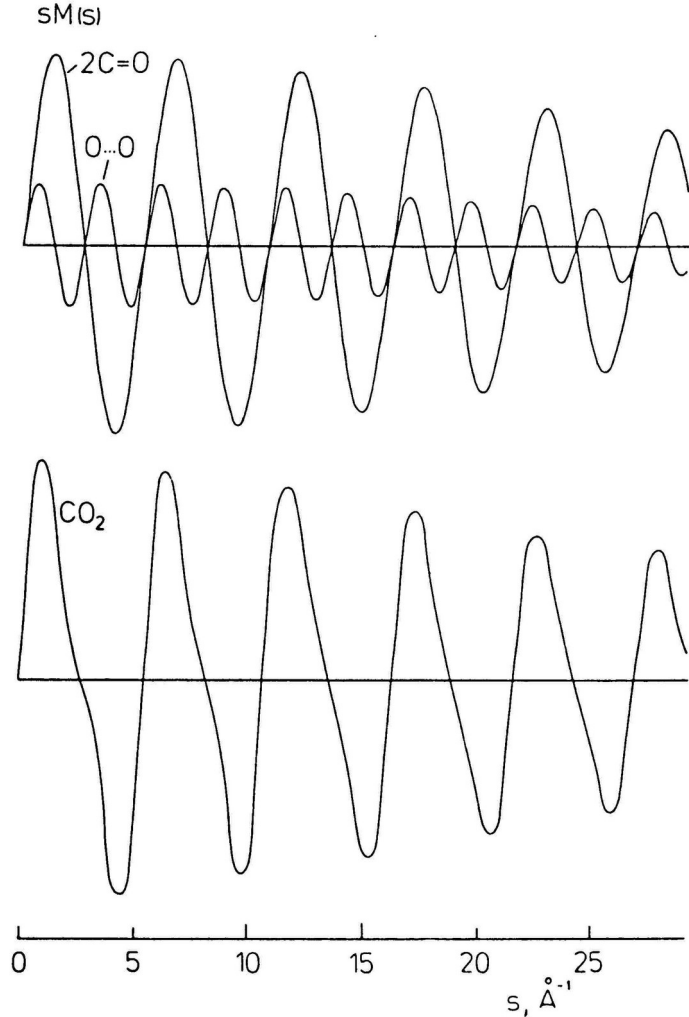
$$r(\text{Cl}\dots\text{Cl}) = 2.8827(6) \text{ \AA}$$

$$l(\text{C}-\text{Cl}) = 0.0483(12) \text{ \AA}$$

$$l(\text{Cl}\dots\text{Cl}) = 0.0715(7) \text{ \AA}$$



Zwei Abstände: CO₂



$$sM(s) =$$

$$2g_{CO} e^{\frac{-l_{CO}^2 s^2}{2}} \sin \frac{(sr_{CO})}{r_{CO}}$$

$$+ g_{OO} e^{\frac{-l_{OO}^2 s^2}{2}} \sin \frac{(sr_{OO})}{r_{OO}}$$

Gemittelte Struktur: CO₂

$$\delta = 2r_a(\text{C-O}) - r_a(\text{O...O})$$

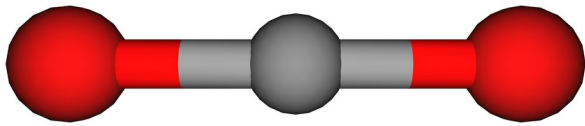
0.0036(5) @ 298 K

0.0059(11) @ 463 K

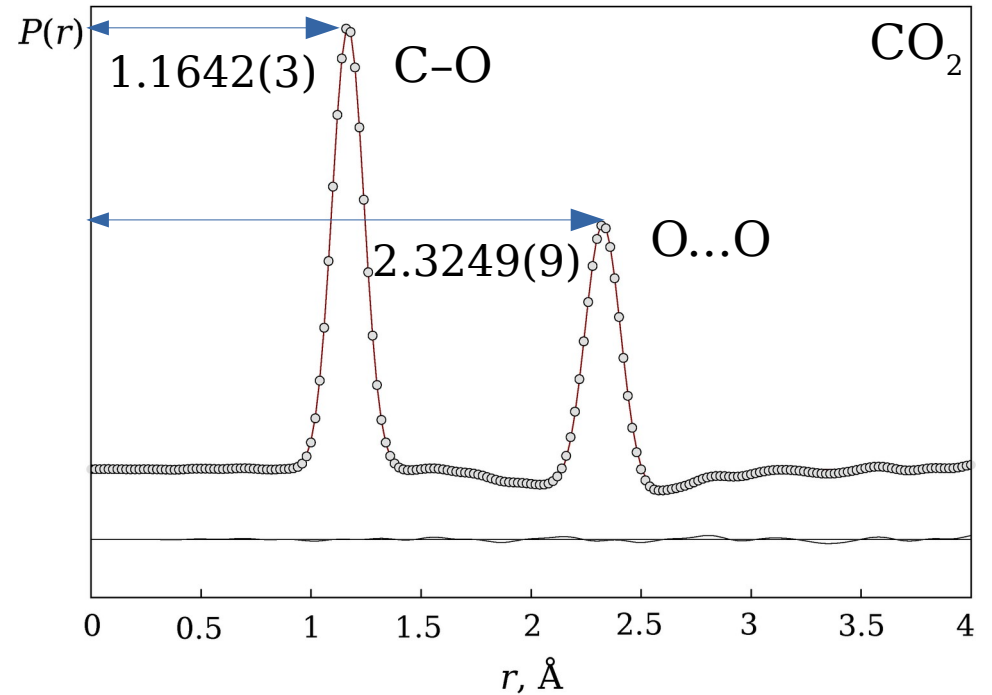
0.0071(8) @ 627 K

0.0078(10) @ 731 K

0.0093(7) @ 937 K



Linear ???



Shrinkage Effekt

$$r_g = \langle r \rangle$$

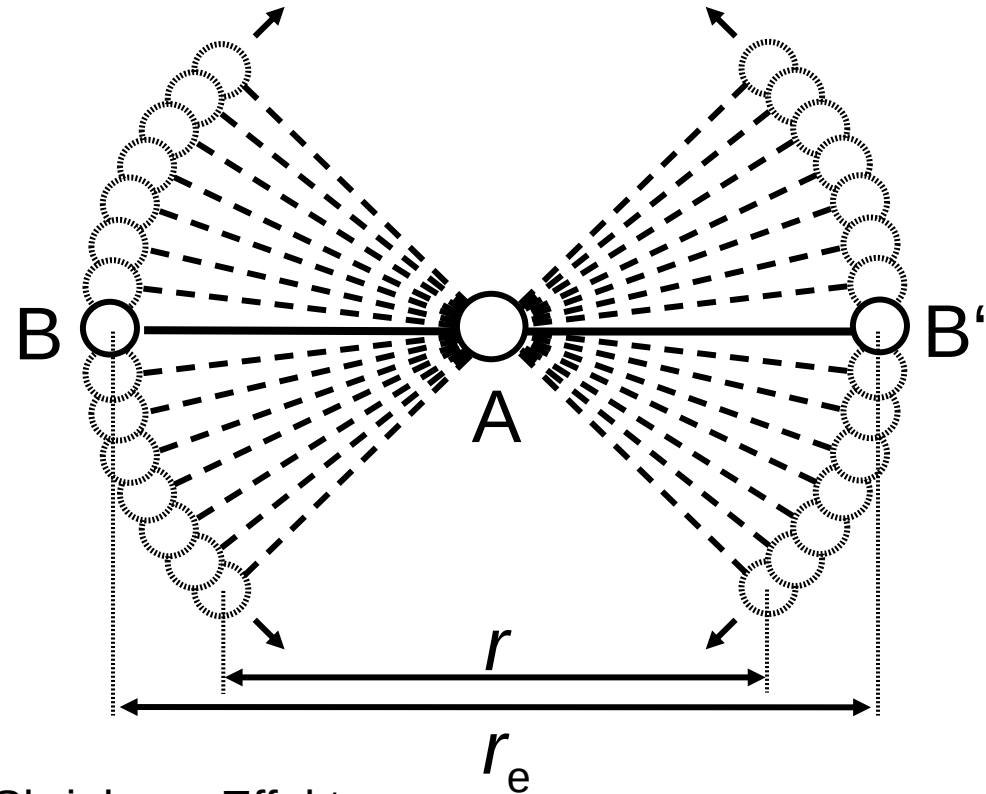
$$r_a = \langle 1/r \rangle^{-1}$$

Beispiel: HgBr_2

$\langle_a(\text{Br-Hg-Br}) \sim 170^\circ$

Korrekturen zu geometrisch
konsistent Strukturen: (r_{h0}, r_{h1}, r_e) :

- Störungstheorie
Krauffelder + XYZ
- Molekulardynamik
Trajektorie



Shrinkage Effekt:

$$r_a(\text{B...B}) < 2r_a(\text{A-B})$$

Atomabstandsparameter

r_a thermisch gemittelter Abstand
direkt aus GED zugänglich

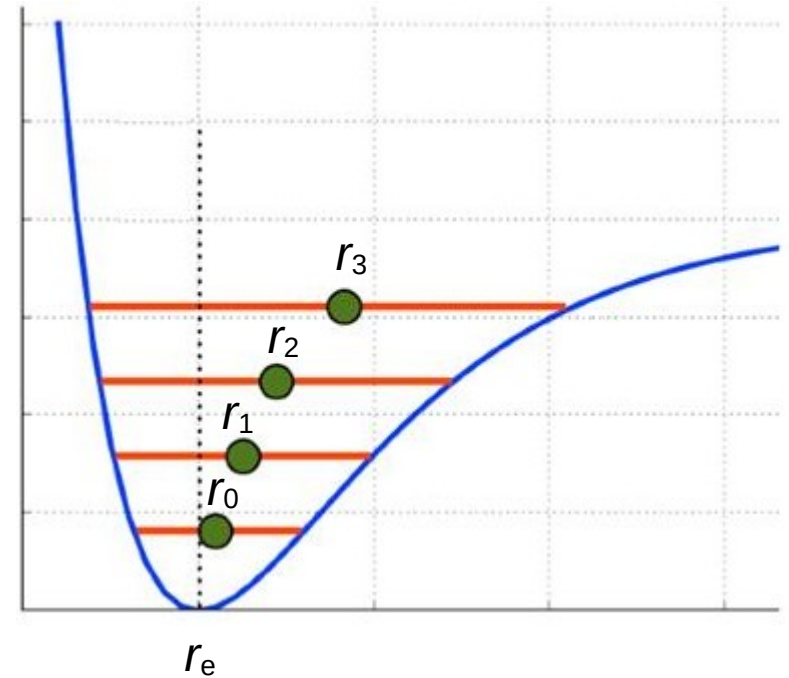
$$r_g = \langle r \rangle_T \quad r_a = \left(\left\langle \frac{1}{r} \right\rangle_T \right)^{-1}$$

r_e Abstand der Atome im Gleichgewicht
(Potentialminimum)

r_g thermisch gemittelter Abstand

r_α Abstand zwischen mittleren Kernpositionen
im thermischen Gleichgewicht bei Temperatur T

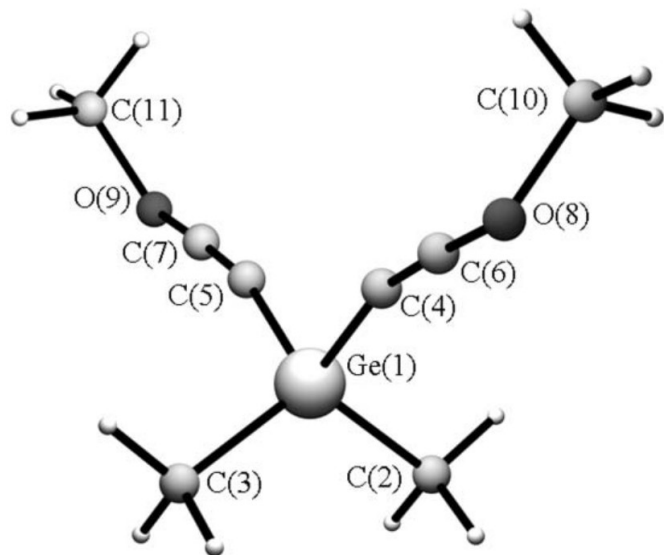
r_α^0, r_z Abstand zwischen mittleren Kernpositionen
im Schwingungsgrundzustand



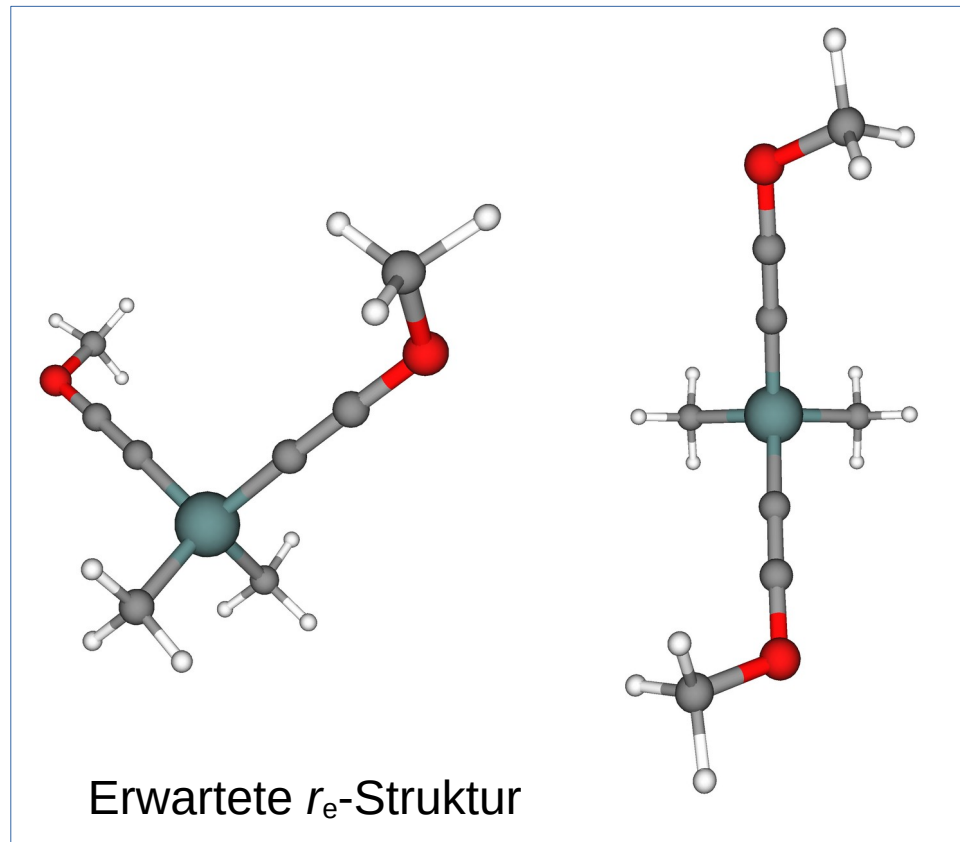
Normalerweise für Bindungen: $r_e < r_\alpha^0 < r_\alpha \approx r_a < r_g$

Thermisch gemittelte Struktur

Dimethyl-bis(methoxyethynyl) germanium



Verfeinert aus GED Daten @ 382 K



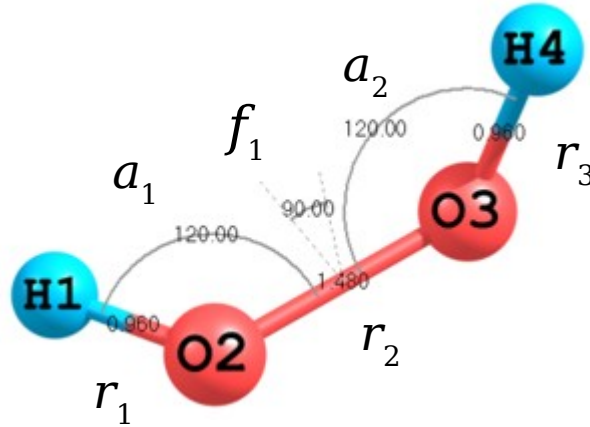
Geometrie Verfeinerung: Z-Matrix

Anzahl Parameter:

$(x,y,z): 3N$

$(r, \angle, \varphi): 3N-6$

$r_{ij}: N(N-1)/2$



```
1 H
2 O 1 r1
3 O 2 r2 1 a1
4 H 3 r3 2 a2 1 f1
Parameter:
r1 = 1.0
r2 = 1.5
r3 = 1.0
a1 = 120.0
a2 = 120.0
f1 = 100.0
```

$(r, \angle, \varphi) \rightarrow (x,y,z) \rightarrow r_{e,ij} \rightarrow r_{a,ij} \rightarrow SM(s)$

Vorteile: direkte Kontrolle für Parameter, Δp fixieren.

Nachteile: keine Kontrolle für abhängige Parameter, sub-optimale Z-Matrizen.

Parameter Verfeinerung

Methode der kleinsten Quadrate:

$$Q = \sum [sM(s)_{\text{exper}} - sM(s)_{\text{modell}}]^2 \rightarrow \min$$

Mit Regularisierung:

$$Q = \sum [sM(s)_{\text{exper}} - sM(s)_{\text{modell}}]^2 + \alpha \times \sum [p_0 - p_{\text{modell}}]^2 \rightarrow \min$$

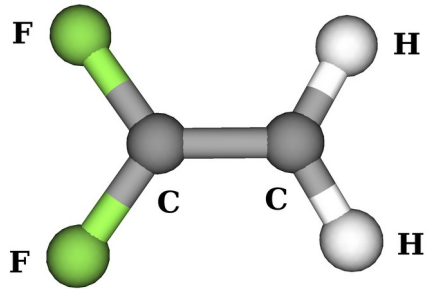
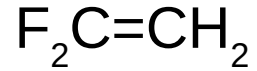
Mit zusätzlichen Daten:

$$\begin{aligned} Q = & \sum [sM(s)_{\text{exper}} - sM(s)_{\text{modell}}]^2 \\ & + \alpha \times \sum [B_{\text{exper}} - B_{\text{modell}}]^2 \\ & + \beta \times \sum [v_{\text{exper}} - v_{\text{modell}}]^2 \\ & + \gamma \times \sum [D_{\text{exper}} - D_{\text{modell}}]^2 \rightarrow \min \end{aligned}$$

- Rotationskonstanten
- Schwingungsfrequenzen
- Dipolar Coupling Konstanten

α, β, γ – Gewichte.

GED + MW



Probleme:

MW: ^{19}F , C \rightarrow Schwerpunkt.

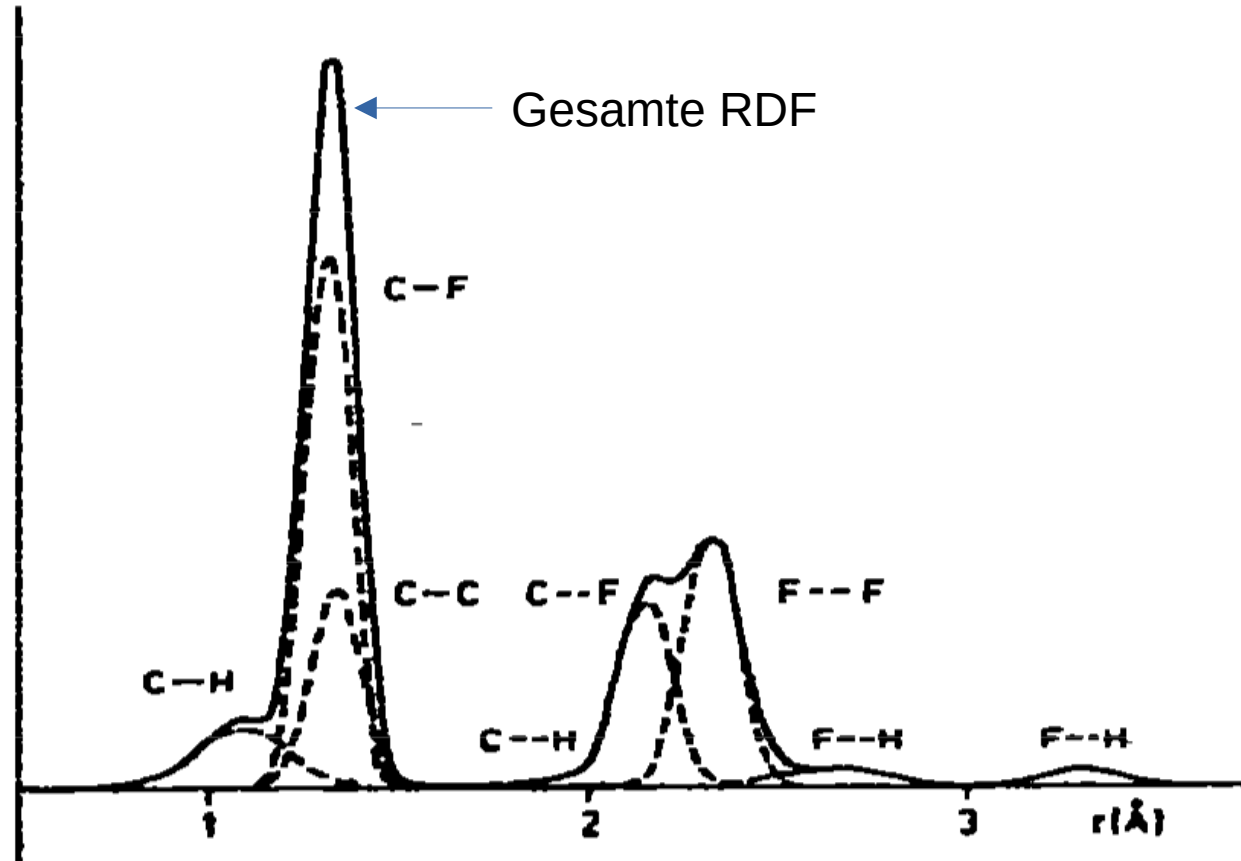
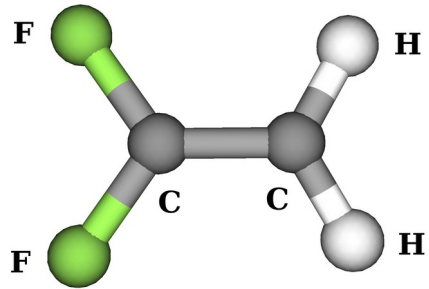
GED: Korrelation $r(\text{C}=\text{C})/r(\text{C}-\text{F})$

GED+MW:

$$r_g(\text{C}=\text{C}) = 1.340(6) \text{ \AA}$$

$$r_g(\text{C}-\text{F}) = 1.315(3) \text{ \AA}$$

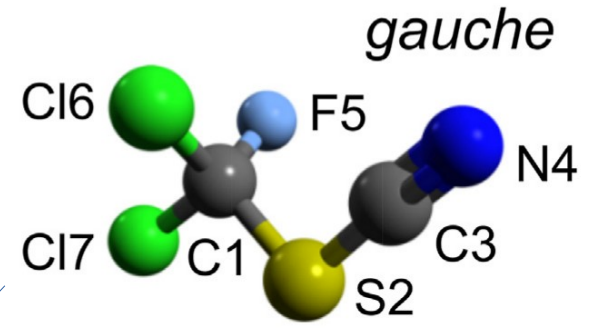
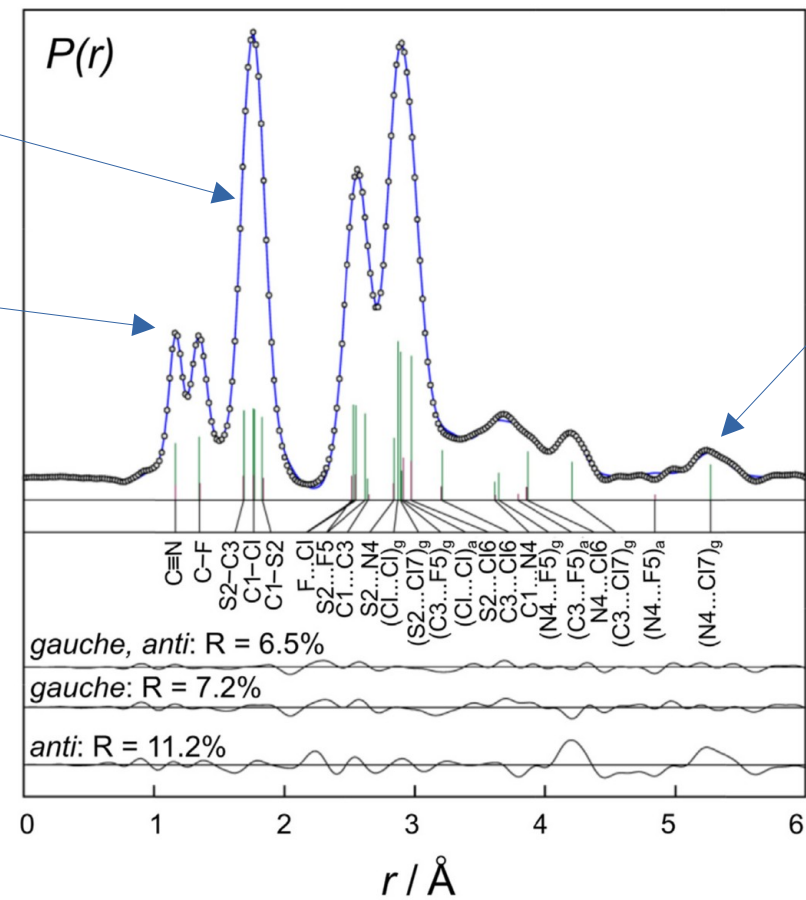
RDF Auflösung



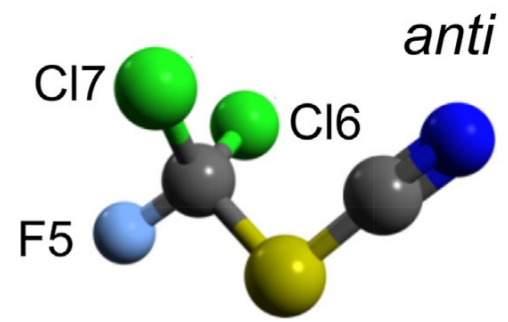
RDF Auflösung

$r(\text{C-S}), r(\text{C-Cl})$ sind korreliert.

$r(\text{C}\equiv\text{N})$ und $r(\text{C-F})$ sind leicht unabhängig verfeinerbar.

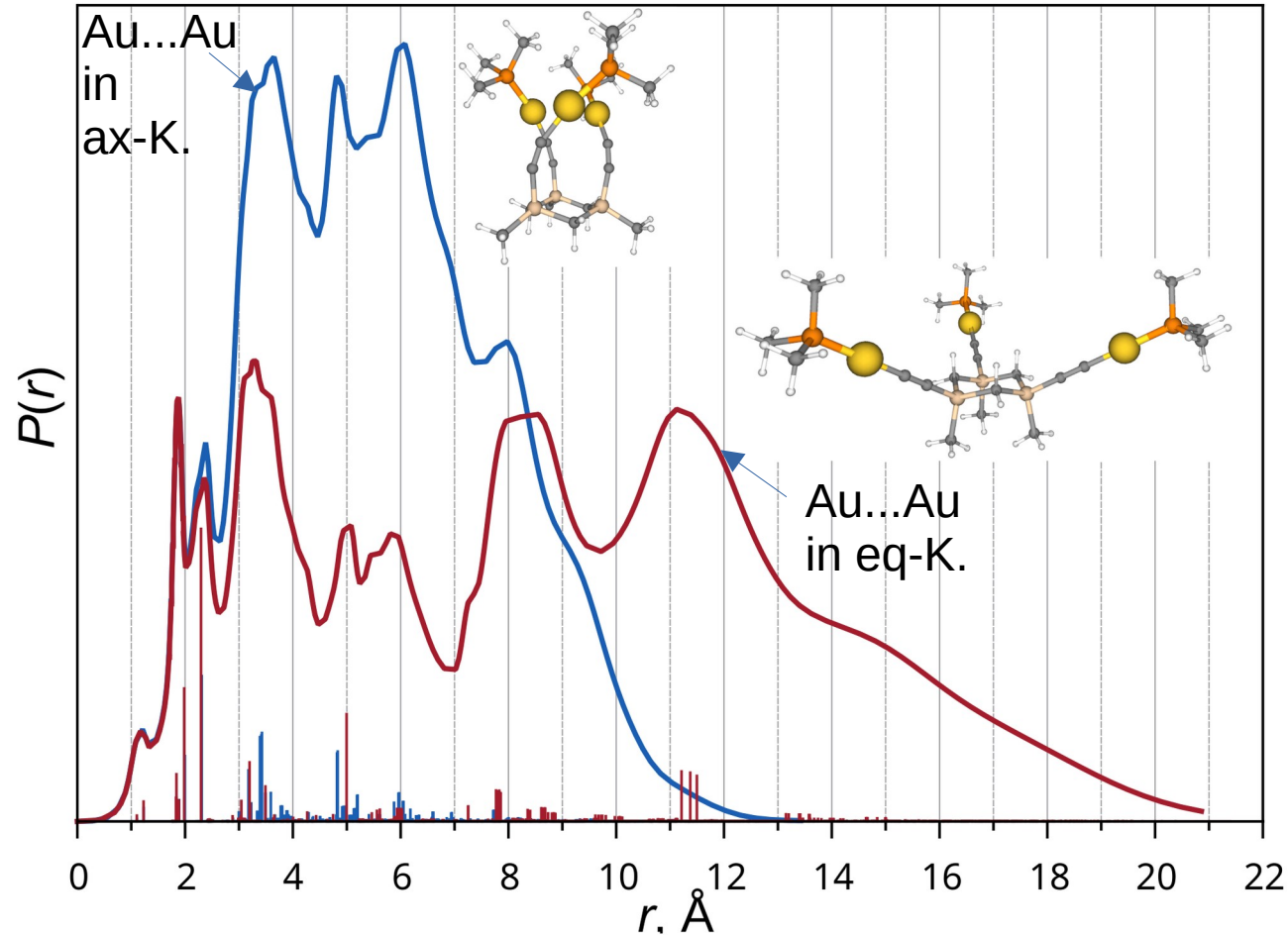


Definitiv in der Gasphase

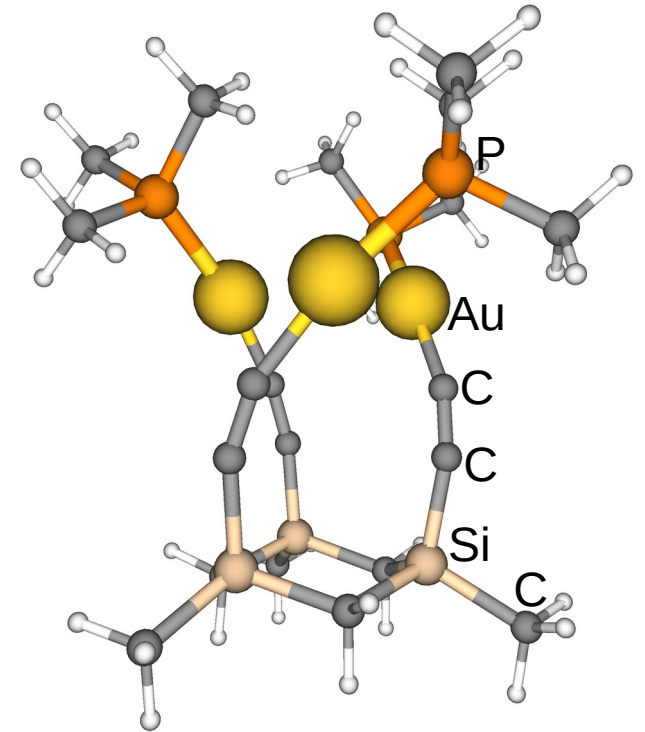


RDF Modellierung

Peter Heinrichs: 1,3,5-Me₃-1,3,5-(C≡CAuPMe₃)₃-1,3,5-trisilacyclohexan



Wegen Streuung an Au...Au muss Konformationsproblem leicht lösbar sein!

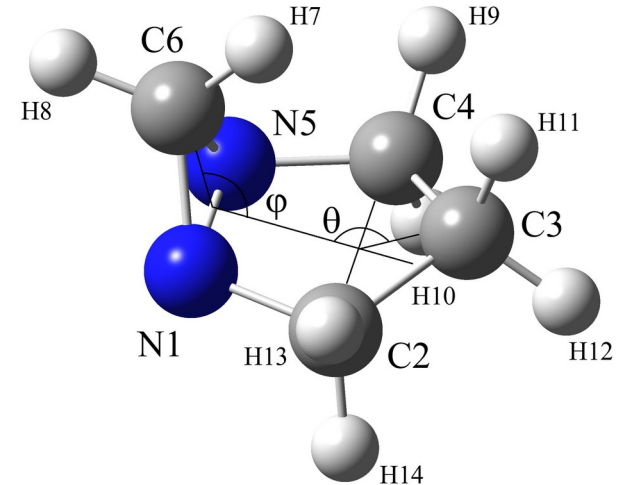
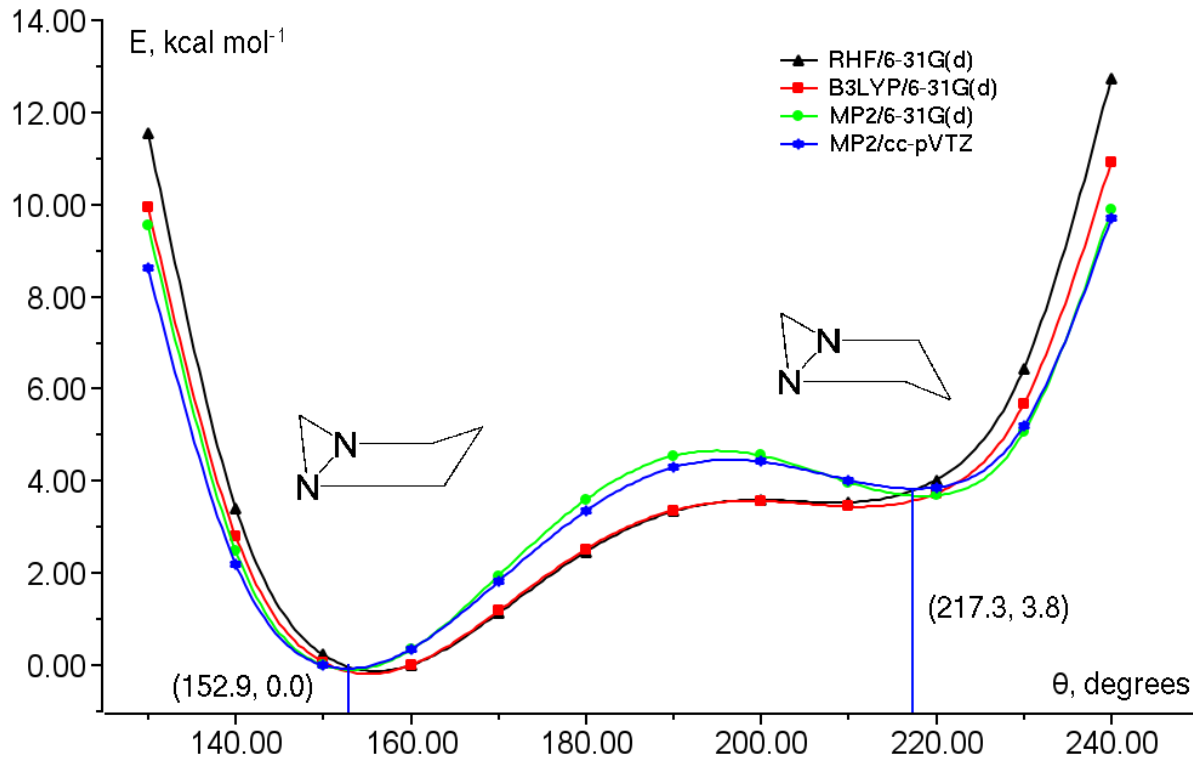


Konformerverhältnisse

$$sM(s)_{total} = x_1 \times sM(s)_{mol1} + x_2 \times sM(s)_{mol2}$$
$$x_1 + x_2 = 1$$

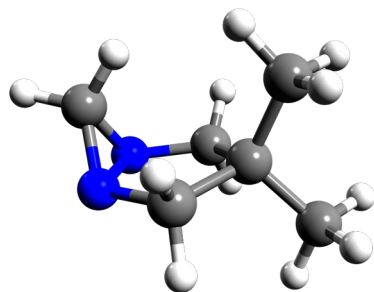
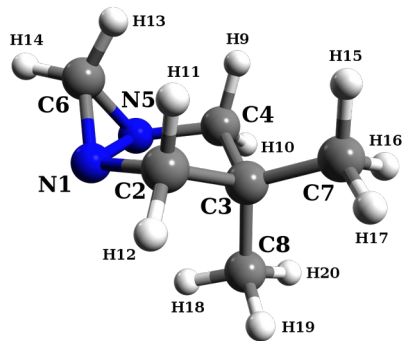
1,5-diazabicyclo[3.1.0]hexan (DABH)

J. Phys. Chem. A, 112 (2008) 5243



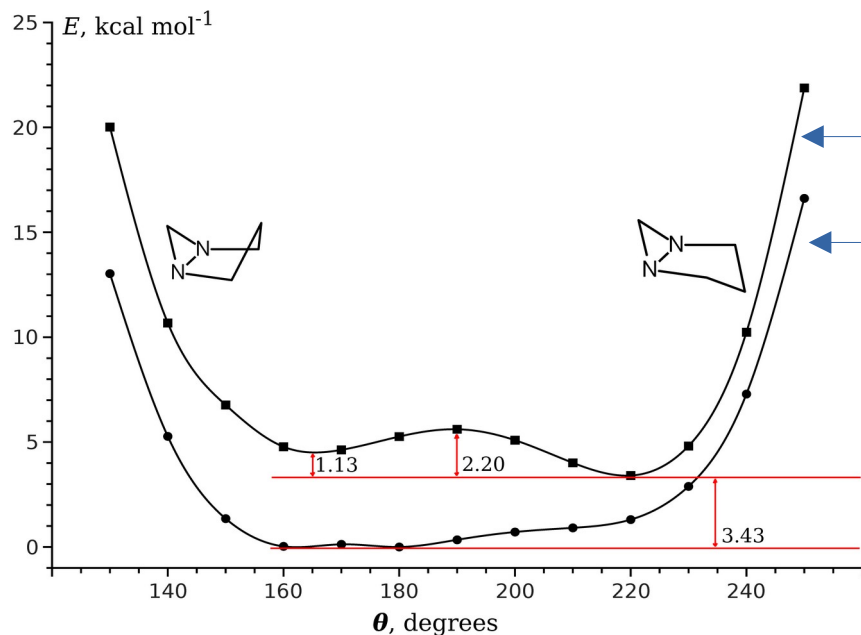
Nur Wanne @ 293 K

Konformerverhältnis: 3,3-Me₂-DABH



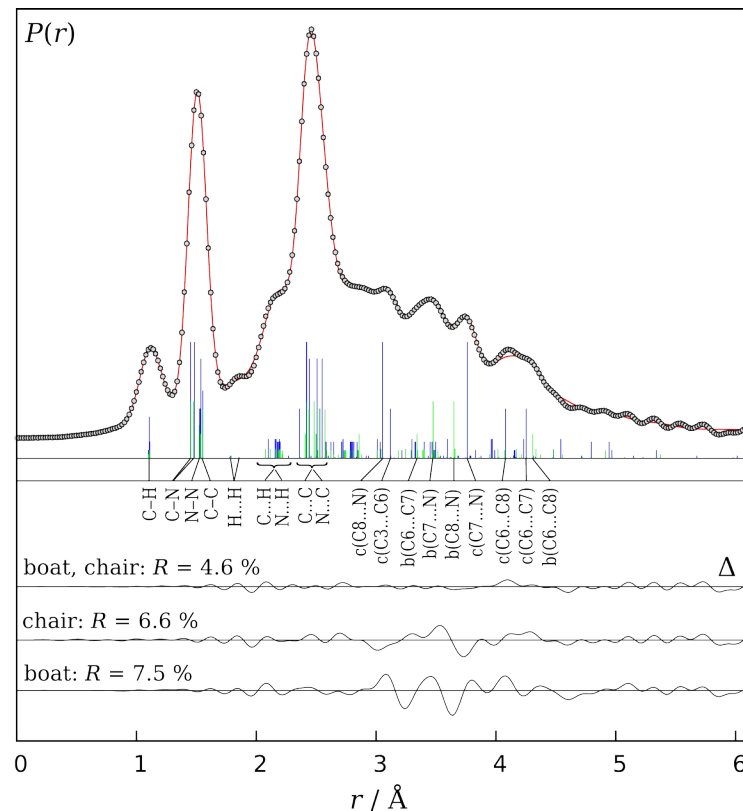
J. Phys. Chem. A, 119 (2015) 10871

32(8) % Wanne,
68(8) % Sessel
@ 293 K

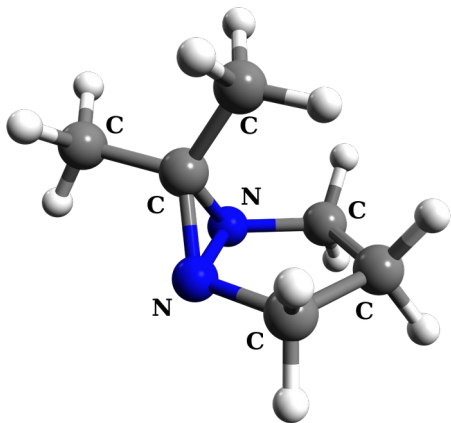


3,3-Me₂-DABH

6,6-Me₂-DABH



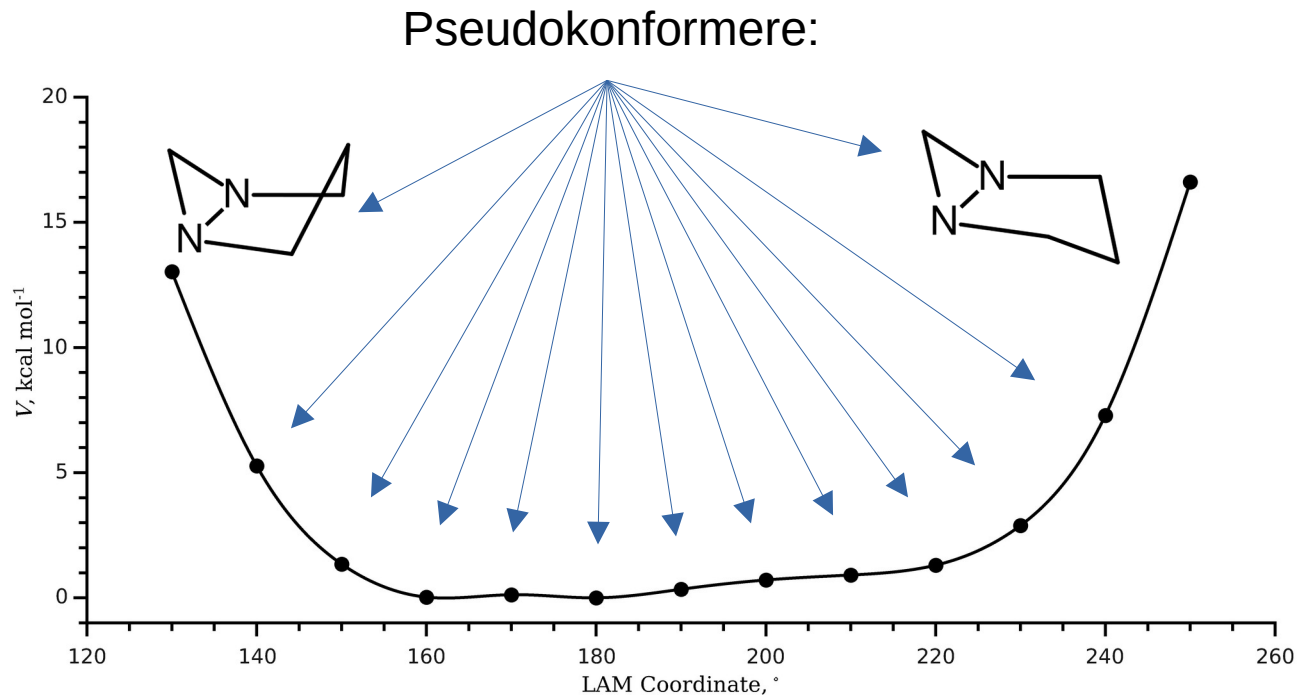
Dynamisches Modell: 6,6-Me₂-DABH



$$sM(s)_{tot} = \int P(\phi) sM(\phi, r, l) d\phi$$

Boltzmann Verteilung:

$$P(\phi) \sim e^{\frac{-V(\phi)}{kT}}$$



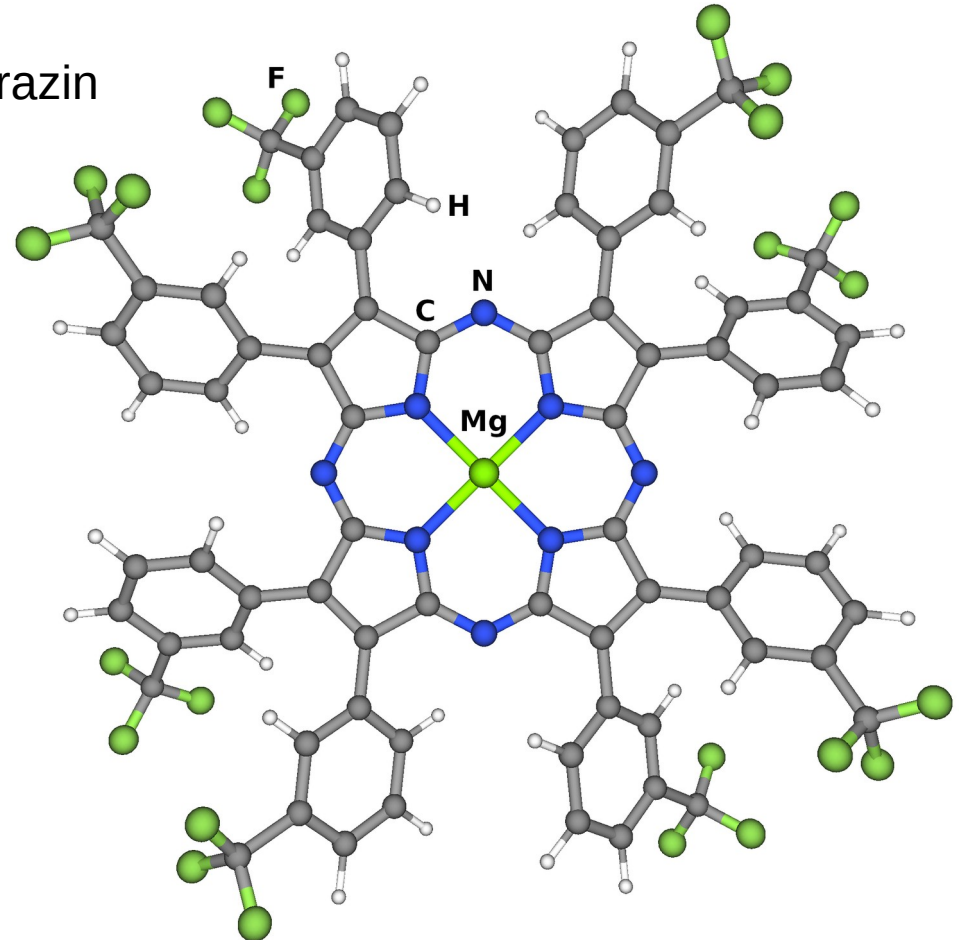
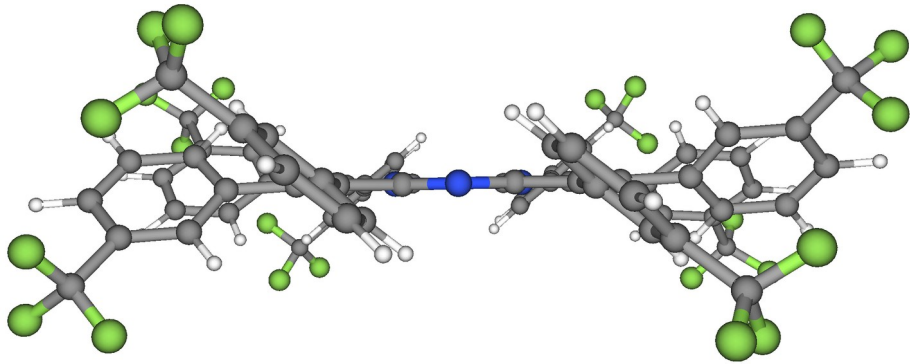
J. Phys. Chem. A, 119 (2015) 10871

Größte Moleküle in GED

Magnesium octa(m-trifluoromethylphenyl)porphyrazin

Symmetrie: D_4 (50 geom. Freiheitsgrade)

$r_{\max} \approx 20 \text{ \AA}$



Y. A. Zhabanov, A. V. Zakharov, N. I. Giricheva, S. A. Shlykov, O. I. Koifman, G. V. Girichev, *J. Mol. Struct.* 1092 (2015) 104.

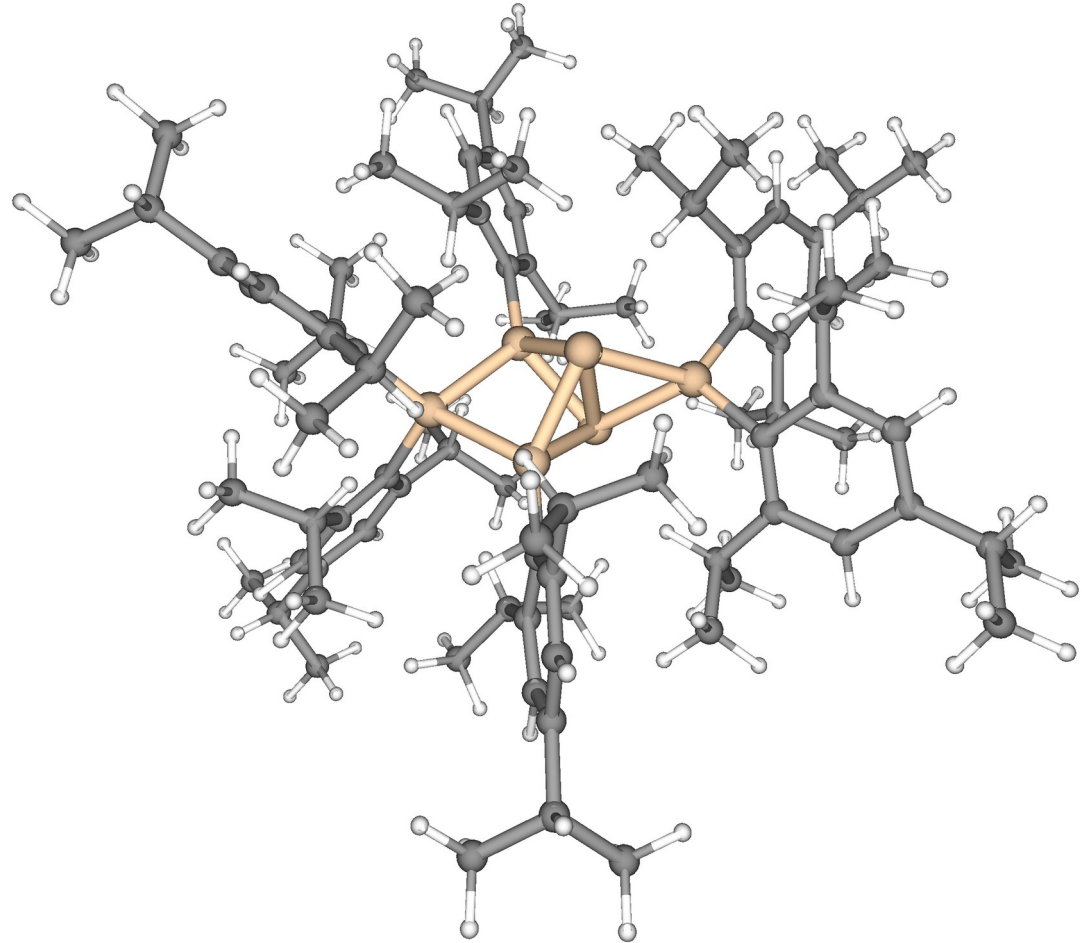
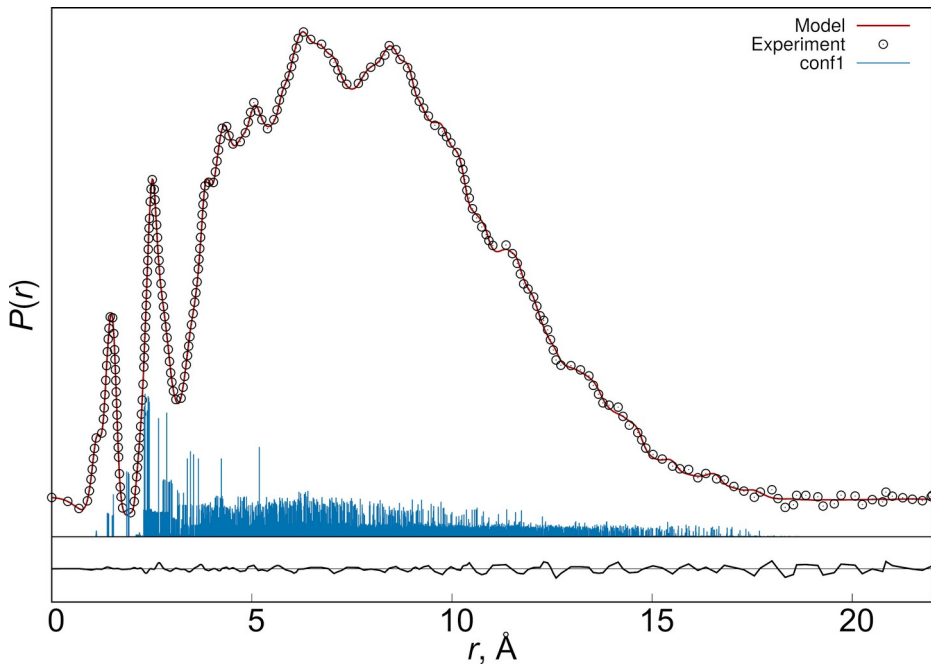
Größte Moleküle in GED

Si₆Tip₆, Tip = 2,4,6-iPr₃C₆H₂

GED @ Uni-Bielefeld

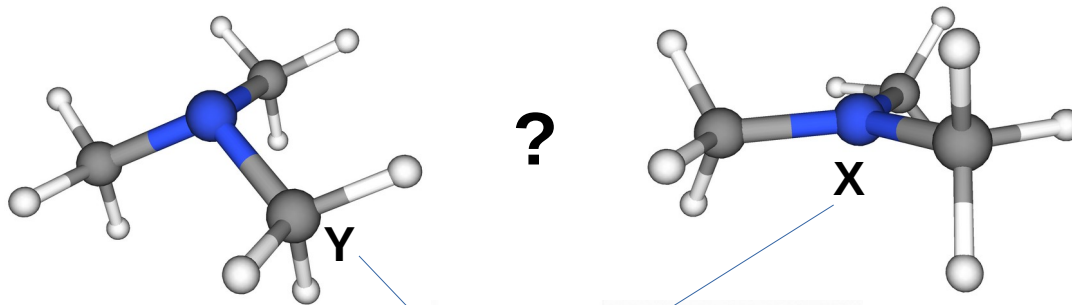
Symmetrie: C₁ (696 geom. Freiheitsgrade)

$r_{\max} \approx 20 \text{ \AA}$



Molekül(e) des Tages

$X(YH_3)_3$:
flach oder pyramidal?

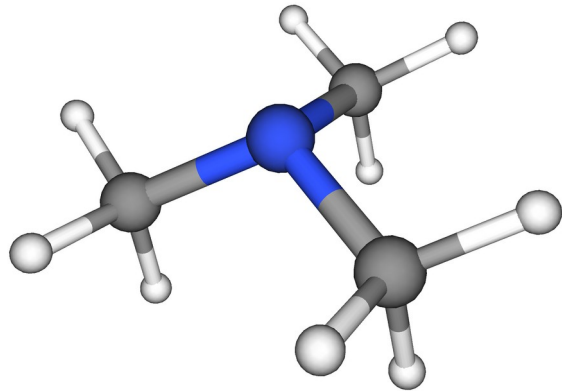


| | | | | | | | | | | | | | | | | | | |
|---|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| | 1* | | | | | | | | | | | | | | | | | 18 |
| 1 | 1 H | 2 | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 He |
| 2 | 3 Li | 4 Be | | | | | | | | | | | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| 3 | 11 Na | 12 Mg | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 4 | 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 5 | 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 6 | 55 Cs | 56 Ba | 57 La | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 Tl | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 7 | 87 Fr | 88 Ra | 89 Ac | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 Cn | 113 Nh | 114 Fl | 115 Mc | 116 Lv | 117 Ts | 118 Og |

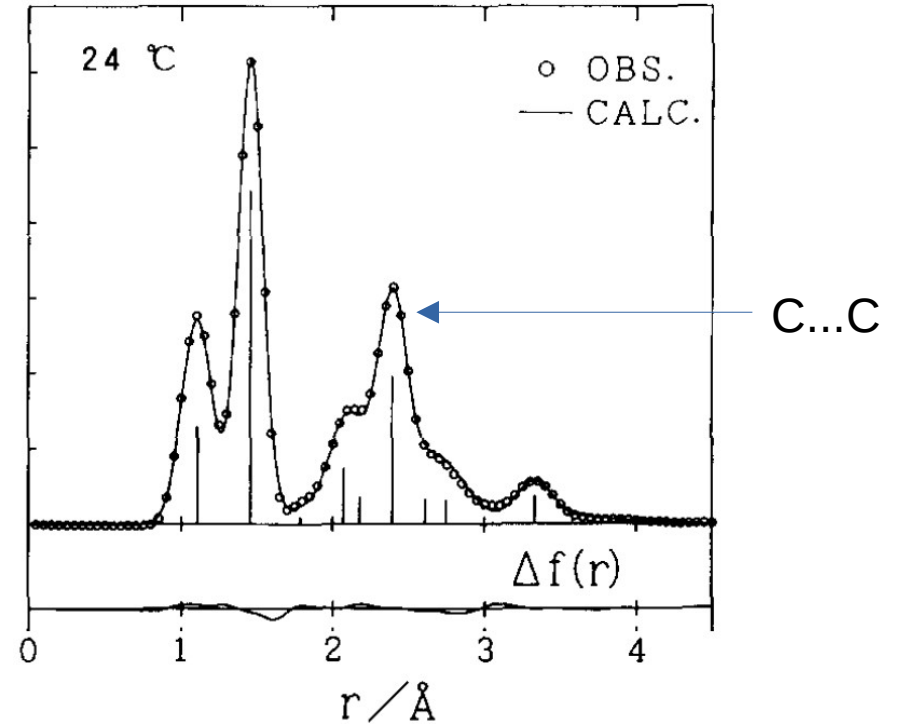
Trimethylamin $\text{N}(\text{CH}_3)_3$

Wollrab et al. (1969) MW: pyramidal

Fujiwara et al, (1995) GED: pyramidal



Erklärung: VSEPR-Modell

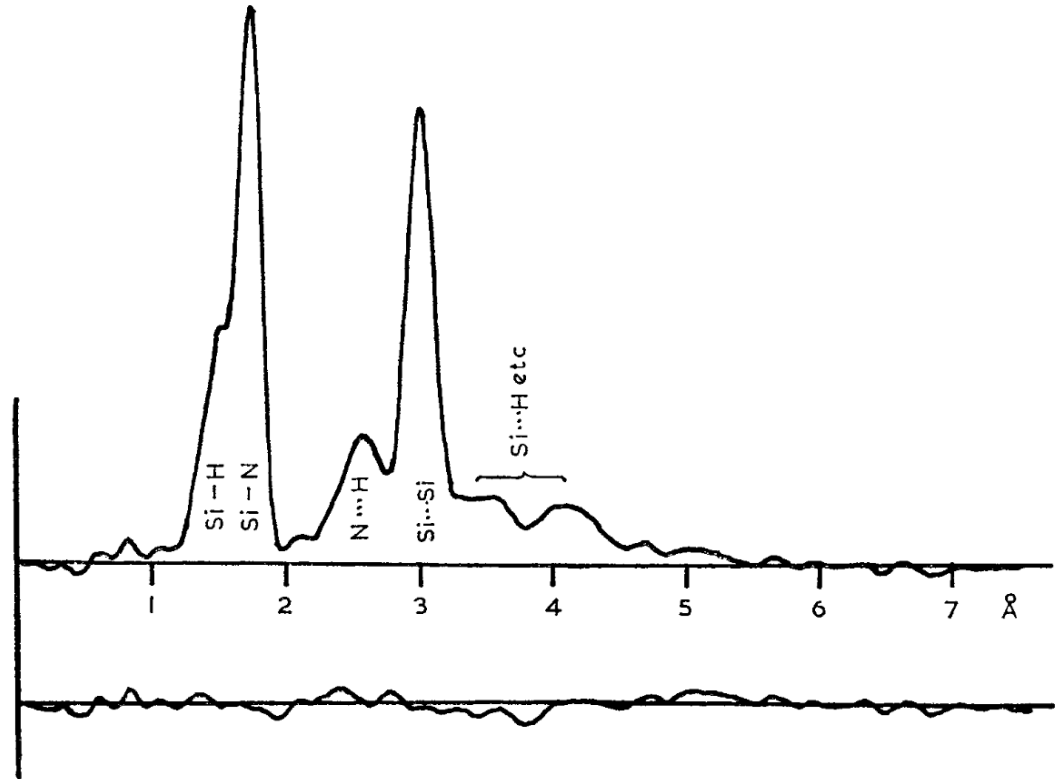
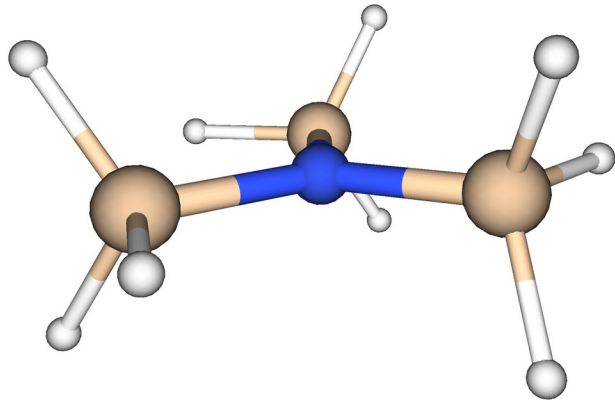


Trisilylamin $N(\text{SiH}_3)_3$

Hedberg (1955) GED: **flach!**

Ebsworth et al. (1958) IR+Raman: **flach**

Beagley et al. (1970) GED: **flach**



Trisilylphosphin $P(\text{SiH}_3)_3$

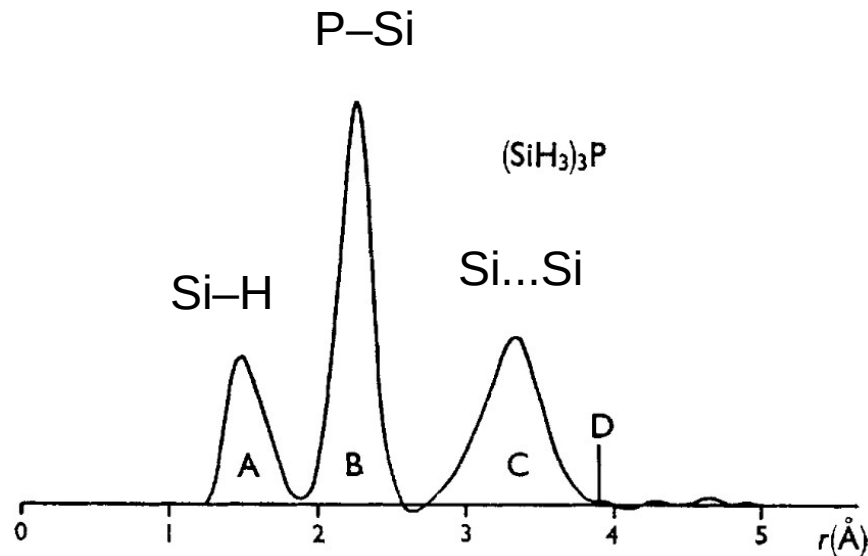
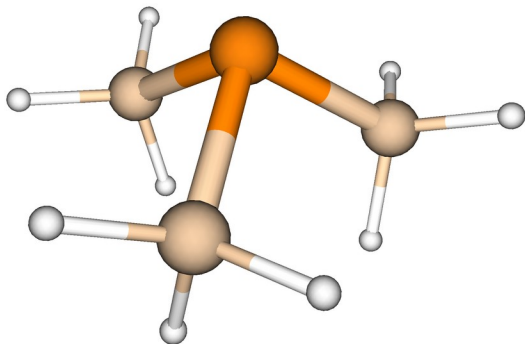
Vibrational Spectra of Trisilylphosphine: Evidence for Planar PSi_3 Structure

By G. DAVIDSON, E. A. V. EBSWORTH, G. M. SHELDRIK, and L. A. WOODWARD

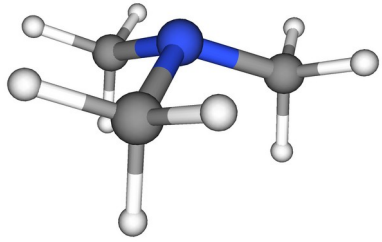
[*Inorganic Chemistry Laboratory, Oxford University (G.D. and L.A.W.), and University Chemical Laboratory, Cambridge (E.A.V.E. and G.M.S.)*]

Davidson et al. (1965) IR+Raman: **flach** (!?)

Beagley et al. (1967, 1977) GED: **pyramidal**,
 $\alpha(\text{Si-P-Si}) = 96.8(5)^\circ$



Natural bond orbital (NBO), Ladungen

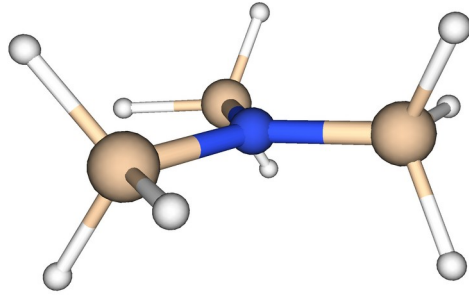


$\text{N}(\text{CH}_3)_3$:

$$q(\text{N}) = -0.5$$

$$q(\text{C}) = -0.4$$

$$q(\text{H}) = 0.2$$

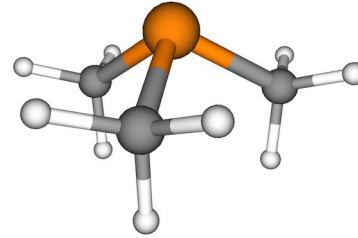


$\text{N}(\text{SiH}_3)_3$:

$$q(\text{N}) = -1.7$$

$$q(\text{Si}) = 1.1$$

$$q(\text{H}) = -0.2$$

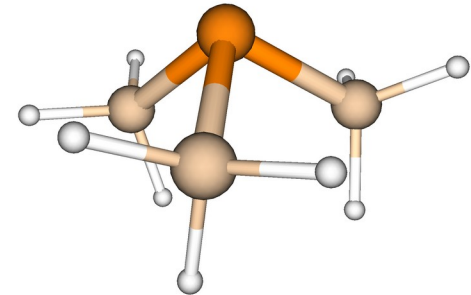


$\text{P}(\text{CH}_3)_3$:

$$q(\text{P}) = 0.7$$

$$q(\text{C}) = -0.9$$

$$q(\text{H}) = 0.2$$



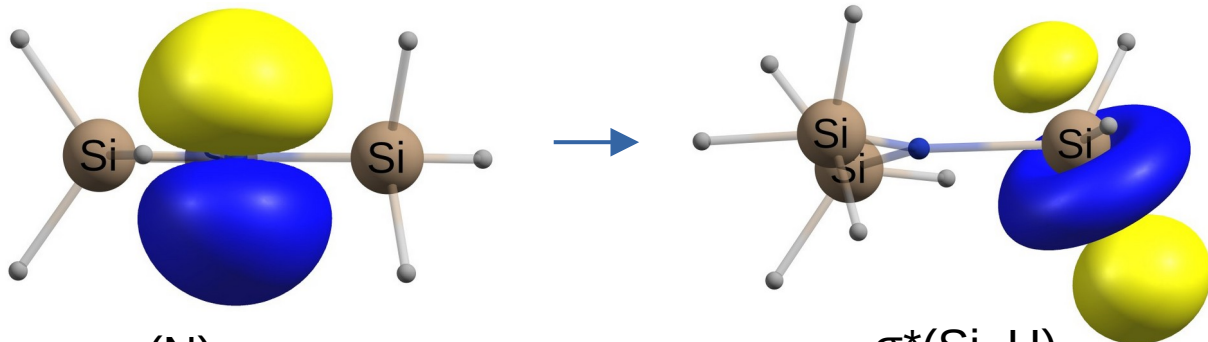
$\text{P}(\text{SiH}_3)_3$:

$$q(\text{P}) = -0.5$$

$$q(\text{Si}) = 0.6$$

$$q(\text{H}) = -0.1$$

N(SiH₃)₃: NBO Wechselwirkungen



$n(N)$
(1.85 e)

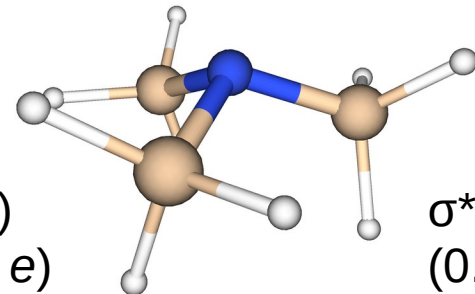
$\sigma^*(Si-H)$
(0.04 e)

6 x $n(N) \rightarrow \sigma^*(Si-H)$ $E^{(2)} = -6.0$ kcal/mol
 3 x $n(N) \rightarrow \sigma^*(Si-H)$ < 0.5 kcal/mol

NLMO dE zur sterischen Energie [kcal/mol]:

$n(N)$ -1.4
 $\sigma(N-Si)$ 59.5 (je Orb.)
 $\sigma(Si-H)$ 4.8 (je Orb., gemittelt)
 Gesamt: **219.9** kcal/mol

Gerechnet für $\alpha(Si-N-Si)=110.0^\circ$
 $\Delta E = +6.5$ kcal/mol



$n(N)$
(1.86 e)

$\sigma^*(Si-H)$
(0.04 e)

3 x $n(N) \rightarrow \sigma^*(Si-H)$ -6.3 kcal/mol
 3 x $n(N) \rightarrow \sigma^*(Si-H)$ -3.5 kcal/mol
 3 x $n(N) \rightarrow \sigma^*(Si-H)$ < 0.5 kcal/mol

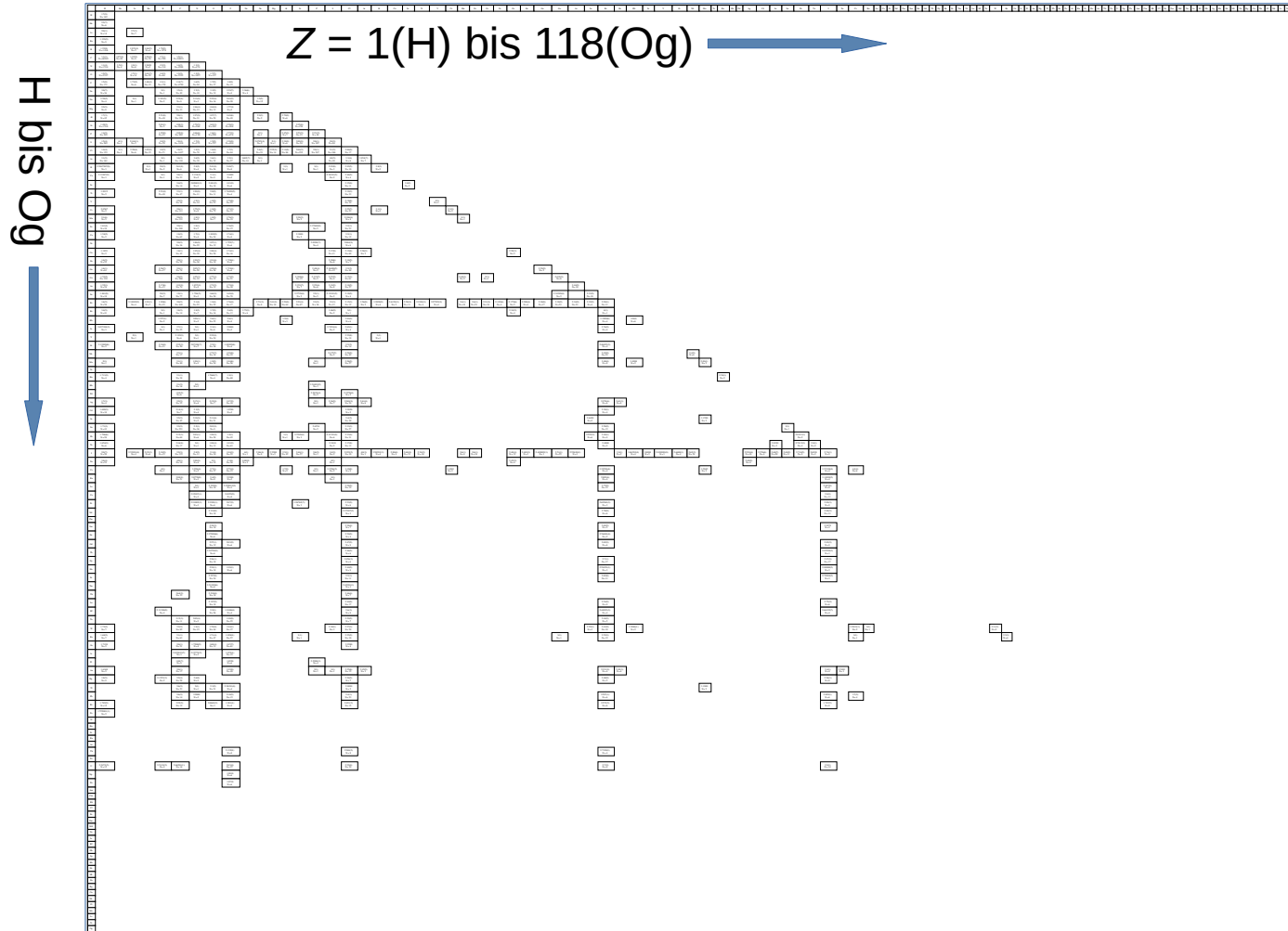
NLMO dE zur sterischen Energie:

$n(N)$ -13.3
 $\sigma(N-Si)$ 62.0 (je Orb.)
 $\sigma(Si-H)$ 6.0 (je Orb., gemittelt)
 Gesamt: **226.7** kcal/mol

$\alpha(X-Y-X)$: **GED** und [Theorie]

| | X = CH ₃ | SiH ₃ | GeH ₃ | SnH ₃ | PbH ₃ |
|-------|----------------------------|----------------------------|--------------------------|------------------|------------------|
| Y = N | 110.6(2) [111.4] | 119.7(3) [120.0] | 120.0 [119.5] | [120.0] | [115.4] |
| P | 98.8(3) [99.4] | 96.8(5) [95.2] | 95.7(5) [96.2] | [95.6] | [95.7] |
| As | 96.1(5) [97.0] | 94.1(2) [92.5] | [93.7] | [92.9] | [93.3] |
| Sb | 94.1(5) [94.5] | 89.0(3) [89.4] | [90.6] | [89.4] | [90.3] |
| Bi | 97.1(10) [93.0] | [87.1] | [88.8] | [87.4] | [88.6] |

Experimentelle Daten für Gasphase



Quelle:
MOGADOC 2023
(10.3K Strukturen)

Quellen/Literatur

- D. W. H. Rankin, N. W. Mitzel, C. A. Morrison, *Structural Methods in Molecular Inorganic Chemistry*, John Wiley & Sons, Chichester, 2013.
- G. A. Sim, L. E. Sutton, Eds., *Molecular Structure by Diffraction Methods: Volumes 1 – 6*, The Royal Society Of Chemistry, 1973 – 1977.
- J. C. Lindon, Ed., *Encyclopedia of Spectroscopy and Spectrometry*, Academic Press, Amsterdam, Boston, 2010.